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# Analysis of Water-Soluble Organics

Little (Arthur D.), Inc., Cambridge, MA

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# ANALYSIS OF WATER-SOLUBLE ORGANICS

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**16. ABSTRACT** The report gives results of several analytical procedures for separating and detecting non-extractable water-soluble organic material, including low molecular weight acids, alcohols, ketones, and other categories of compounds. (There are many ways to analyze hydrophobic extractable organics, but few for hydrophilic materials.) An analytical scheme has been developed that utilizes several chromatographic procedures standards with known water-soluble compounds from a variety of compound categories. The retention time data provide elution profiles for each compound category which can be exploited to characterize an unknown mixture. The precision and accuracy data for each compound analyzed using these chromatographic systems are reported. Additional areas described in the report include: (1) the application of total organic carbon/freeze drying to monitor and concentrate non-extractable water-soluble alcohols from water; (2) the detection of specific compound categories using colorimetric procedures such as the Anthrone and Molisch tests; (3) the application of Level 1 procedures using water-soluble model compounds; (4) the evaluation of gas chromatography/Fourier transformation infrared as a viable way to analyze hydrophilic materials in fractions obtained from the Level 1 fractionation scheme; and (5) an analytical way to detect linear alkylbenzene sulfonates.

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|---|---|---|
| Pollution | Pollution Control | 13B |
| Organic Compounds | Stationary Sources | 07C |
| Solubility | Hydrophilic Material | 07D |
| Analyzing | | 14B |

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## TABLE OF CONTENTS

Page

LIST OF FIGURES v

LIST OF TABLES vii

GLOSSARY OF TERMS AND ABBREVIATIONS ix

ACKNOWLEDGEMENT x

ABSTRACT xi

PART I: SEPARATION AND DETECTION OF WATER SOLUBLE ORGANICS BY DIRECT AQUEOUS INJECTION 1

- 1. Summary 1
- 2. Introduction 3
- 3. Literature 4
- 4. Background 15
- 5. Experimental 21
  - A. Experimental Approach 21
  - B. Experimental Details 26
    - 1. Materials 26
    - 2. Instruments 27
    - 3. Analytical Method - Direct Aqueous Injection 27
- 6. Results and Discussion 30
  - 1. Elution Profiles 31
  - 2. DAI of Test Mixture 63
  - 3. DAI of Unknown Environmental Samples and QC Data 72
  - 4. DAI Summary 76
  - 5. DAI Conclusions 79

## TABLE OF CONTENTS (CONTINUED)

Page

PART II: ADDITIONAL AREAS OF INVESTIGATION 80

1. Summary 80
2. Introduction 82
3. Experimental 85
    A. Experimental Details 85
        1. Materials 85
        2. Instruments 86
        3. Analytical Methods 86
4. Results and Discussions 92
    A. TOC and HPLC Measurements, Sample Handling 92
    B. Concentration of Water Soluble Organic Alcohols by Freeze Drying 100
    C. Level 1 Application, GC/FTIR 101
    D. Colorimetric Detection Systems 107
    E. Specific Analytical Method for Linear Alkylbenzene Sulfonates 110
5. Conclusions for Part II Investigations 119

REFERENCES 121

APPENDIX 1 123

APPENDIX 2 125

APPENDIX 3 144

APPENDIX 4 149

## LIST OF FIGURES

| | | Page |
|---|---|---|
| 1 | Classification of Dissolved Organic Carbon (DOC) | 6 |
| 2 | Illustration of the Comprehensive Analysis for Organics in Water | 16 |
| 3 | Elution Profile for HPLC System with RP-2 Column | 34 |
| 4 | Elution Profile for HPLC System with E-125 Column | 35 |
| 5 | Elution Profile for HPLC System with C18 Column | 36 |
| 6 | Elution Profile for HPLC System with Phenyl Column | 37 |
| 7 | Elution Profile for GC System with Tenax Column | 38 |
| 8 | Elution Profile for Acids | 39 |
| 9 | Elution Profile for Alcohols | 40 |
| 10 | Elution Profile for Aldehydes | 41 |
| 11 | Elution Profile for Amino Acids | 42 |
| 12 | Elution Profile for Carbohydrates | 43 |
| 13 | Elution Profile for Glycols | 44 |
| 14 | Elution Profile for Ketones | 45 |
| 15 | Elution Profile for Phenols | 46 |
| 16 | Elution Profile for Amines | 47 |
| 17 | L-Proline Calibration Curve | 61 |
| 18 | Propionic Acid Calibration Curve | 62 |
| 19 | Blank Grid for Preparing Retention Time Overlay | 68 |
| 20 | Example of Overlay Pattern for Unknown Sample Mixture | 69 |
| 21 | Overlay of Sample Retention Times (Figure 20) onto Elution Profiles for Alcohols Category (Figure 9) | 70 |
| 22 | Overlay of Sample Retention Times (Figure 20) onto Elution Profile for Aldehydes (Figure 10) | 71 |

10 Lines to End of Typing Area

## LIST OF FIGURES

| | | Page |
|---|---|---|
| 23 | HPLC of Alcohol Mix | 94 |
| 24 | HPLC of Glycol Mix | 95 |
| 25 | Extraction/Isolation of LAS from a Complex Aqueous Matrix | 111 |
| 26 | Chromatograms of LAS | 114 |
| 27 | Sample Chromatograms | 116 |
| 28 | Calibration Curve of LAS | 117 |

10 Lines
to End of
Typing Area

For Page Numbering

ADL-064 (6) 300M

## LIST OF TABLES

Page

1 Intractable Model Compounds Used in MAS 10

2 Summary of the MAS for Intractable Organics 13

3 Illustrative Values of Solvent: Water Partition Coefficients 18

4 Comparison of Calculated Recoveries with Those Determined by Webb 19

5 Water Soluble Organic Model Compounds 22

6 Sample Analysis of Water Soluble Organics by Direct Aqueous Injection 25

7 HPLC Chromatographic Systems for Direct Aqueous Injection 28

8 GC/FID System for Direct Aqueous Injection 29

9 Retention Time Data for Model Compounds 32

10 Concentration Data for Model Compounds 49

11 Linear Regression Data for Chromatographic System RP-2 51

12 Linear Regression Data for Chromatographic System E-125 53

13 Linear Regression Data for Chromatographic System C-18 55

14 Linear Regression Data for Chromatographic System Phenyl 57

15 Linear Regression Data for Chromatographic System Tenax 59

16 Retention Time Data for Test Mixtures 65

17 Compound Categories Identified by Elution Profiles 66

18 Retention Time Data for Environmental Sample 74

19 Quality Control Data 75

20 Chromatographic Systems that Provide Good Separation of Compounds Within Categories 78

10 Lines to End of Typing Area

## LIST OF TABLES (Continued)

Page

21 Additional Areas of Investigation, Part 2 83

22 Concentration Data for Sample Solutions 93

23 Percent Loss on Extraction Calculated from HPLC Data 96

24 Percent Loss Detected by TOC Compared to HPLC 97

25 Comparison of TOC Data to the Concentration of the Samples Prepared 99

26 Compourds Used for Level 1 and GC/FTIR Application 102

27 LC Analysis, Tabulated TCO Concentrations 103

28 Comparison of Water Soluble Compounds/Categories Present in Mixture with Results of Level 1 Analysis 105

29 Results of Colorimetric Tests 109

30 Elution Pattern on Spheadex G-10 113

31 Analysis of LAS in a Complex Aqueous Matrix 118

## Glossary of Terms and Abbreviations

| | |
|---|---|
| DAI | Direct Aqueous Injection |
| DMEG | Discharge Multimedia Environmental Goals |
| DOC | Dissolved Organic Carbon |
| GC | Gas Chromatography |
| GC/FTIR | Gas Chromatography/Fourier Transform Infrared |
| GC/MS | Gas Chromatography/Mass Spectrometry |
| GPC | Gel Permeation Chromatography |
| HPLC | High Performance Liquid Chromatography |
| LAS | Linear Alkylbenzene Sulfonates |
| LRMS | Low Resolution Mass Spectrometry |
| MAS | Master Analytical Scheme |
| MATE | Minimum Acute Toxicity Effluent (MATE≡DMEG) |
| MEG | Multimedia Environmental Goals |
| Mg/L | Parts per Million (ppm) |
| PAT | Purge and Trap |
| PFB | Pentafluorobenzyl bromide |
| QC | Quality Control |
| TCO | Total Chromatographable Organics |
| TOC | Total Organic Carbon |

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# ABSTRACT

There are numerous methods for the analysis of hydrophobic extractable organics but few exist for hydrophilic type materials. Several analytical procedures were investigated in this effort for the separation and detection of "non-extractable" water soluble organic material, including low molecular weight acids, alcohols, ketones and other categories of compounds. An analytical scheme has been developed that utilizes several chromatographic procedures standardized with known water soluble compounds from a variety of compound categories. The retention time data provide elution profiles for each compound category which can be exploited to characterize an unknown mixture. The precision and accuracy data for each compound analyzed using these chromatographic systems are reported.

Additional areas of investigation described in the report include:

- The application of total organic carbon/freeze drying to monitor and concentrate non-extractable water soluble alcohols from water.

- The detection of specific compound categories using colorimetric procedures such as the Anthrone and Molisch tests.

- The application of Level 1 procedures using water soluble model compounds.

- The evaluation of Gas Chromatography/Fourier Transformation Infrared (GC/FTIR) as a viable method for the analysis of hydrophilic materials in fractions obtained from the Level 1 fractionation scheme.

- An analytical method for the separation and detection of linear alkylbenzene sulfonates is presented.

## 1. PROJECT SUMMARY

The objective of this task was to develop analytical methods for the analysis of "non-extractable" water soluble organic material. To date, no analytical methods exist for the comprehensive separation and detection of this category of compounds. Most identified procedures for polar organic material deal only with compounds that will extract into an organic solvent. The procedures described below were developed with a view to obtaining as much information as possilbe about the "non-extractable" water soluble organic content of a given sample. These procedures would complement those presently included in the EPA Level 1[1] and other common organic analysis schemes.

A review of selected current journals and other readily available literature was conducted to obtain information on analytical techniques or methods which would be directly applicable in achieving the objectives of this task. The majority of the cited articles offered solvent extraction as the mechanism of separation for polar organic material from pH-adjusted aqueous media.

Part I of the experimental portion of this task was directed toward the analysis of aqueous solutions of model compounds selected from the non-extractable water soluble organic category. The procedures included direct aqueous injection (DAI) on five High Performance Liquid Chromatographic Systems and one Gas Chromatographic/Flame Ionization Detection System. Part II of the experimental approach addresses additional areas of investigation including the application of compound category colorimetric indicator tests on mixtures of water soluble organics. Methodology for the isolation of the model compounds from the aqueous media was also investigated and included freeze-drying/TOC and modification of the Level 1 scheme in conjunction with GC/FTIR as a method of detection.

The Direct Aqueous Injection (DAI) approach was investigated to determine whether it would provide qualitative and semi-quantitative information for the presence of water soluble organic materials in aqueous matrices. Several model compounds from nine different categories were analyzed on five chrmoatographic systems. The retention time data obtained were used to construct standardized elution profiles. Positive identification of a compound category for an unknown species is made when the retention time of a detected peak falls within the correct retention time window for that category in each chromatographic system.

The model compounds were analyzed over a concentration range of 15 mg/L to 200 mg/L. With few exceptions, the precision of the methods were defined by correlation coefficients greater than 0.998. Detection limits for most compounds were lower than 25 mg/L. DAI approach utilizing the five fold retention time data base shows promise as a screening technique for at least eight of the nine categories of water soluble model compounds investigated.

## 2. INTRODUCTION

The extraction of organic material from an aqueous matrix by liquid/liquid extraction or by adsorption onto carbon and various macroreticular resins has been well documented. The effectiveness of these methods are totally dependent on the tendency of the organic species in question to selectively partition into the organic solvent or sorbent from water. While a majority of organic chemicals are hydrophobic, with high solvent:water partition coefficients, there are also many hydrophilic organic materials that are highly water soluble and have low partition coefficients. These include, but are not limited to, low molecular weight highly polar species: carboxylic acids, alcohols, ketones, and the like. In this work, "water soluble organics" are, by definition, organic materials which are not extractable or are incompletely extracted with organic solvents. The classical separation/concentration procedures mentioned above find little or no application in the separation/detection of these materials. The object of this task was to develop analytical methods for the analysis of "non-extractable" water soluble organic material. These methods would complement those presently included in the EPA Level 1 procedures and other common organic analyses schemes. Ideally, it would be desirable to develop an analytical scheme which could be applied to sample preparation and analysis in a linear fashion. The state-of-the-art at present does not appear to allow the formulation of such a scheme. However, the direct aqueous injection method presented in this report is an approach toward achieving this objective.

## 3. LITERATURE

A substantial portion of the total organic carbon in waste water may be present in the form of polar, "non-extractable" water soluble organics This concept is substantiated in the Phase 1 Source Assessment: Textile Plant Wastewater Toxics Study[3]. The results of the Level 1 chemical analysis of the secondary effluent from several textile plants sampled in this study indicated that the total concentration of methylene chloride extractable organics were 5 to 10 times lower than the total organic carbon had indicated.

Few methods exist for the isolation and concentration of hydrophilic compounds. A review of the current literature was undertaken to identify procedures which might contribute to the development of an analytical classification scheme for water soluble organic materials. A selection of current journals and the data base accumulated under previous current awarness literature searches were the foundation for the literature review.

### Extraction/Concentration

The majority of references for the extraction and concentration of organics from aqueous systems describe alternatives to liquid/liquid extraction for isolation of low concentrations of extractable material by adsorption on carbon, macroreticular resins, and other adsorbents. Among the procedures cited for the separation and concentration of organic material are steam distillation[4], reverse-phase ion pair High Performance Liquid Chromatography[5], and membrane ultrafiltration[6]. These do not appear to have general value for isolation of water soluble organics. Three specific approaches that attempt to deal specifically with the more hydrophilic species are those of Leenheer *et al*[7], Stalling and Co-workers[8] and the EPA Athens Master Analytical Scheme[9]. These are discussed briefly below.

Leenheer *et al*. devised an approach that allows fractionation of organic solutes dissolved in wastewaters into hydrophobic-acid, base, neutral organics and hydrophilic-acid, base, neutral organics. The selective adsorption is achieved by sequentially passing the water sample through a non-ionic macroreticular resin (to adsorb and selectively separate the hydrophobic organic solutes by controlling pH of the solution and the eluent water) and then through cation and anion-exchange resin. The hydrophilic organic bases are selectively adsorbed on a cation exchange resin; the hydrophilic organic acids are adsorbed on an anion exchange resin and the hydrophilic neutrals remain in the aqueous phase.

The general types of materials classified as hydrophobic and hydrophilic are charted in Figure 1. The distinction into hydrophobic and hydrophilic as defined by Leenheer *et al*.is based on k' value, where:

$$k' = \frac{\text{mass of solute sorbed on XAD-8}}{\text{Mass of solute dissolved in water}}.$$

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In the fractionation and desorption scheme described, water systems are used as eluents because the intended ultimate assay method is total organic carbon analysis, thus any organic solvent used would be an interference.

In order to meet the detection requirements of this analysis, a 200 mL aqueous sample with a Dissolved Organic Carbon (DOC) content of 5-25 mg/L is processed.

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## CLASSIFICATION OF DISSOLVED ORGANIC CARBON

| | | | Compound Types |
|---|---|---|---|
| DISSOLVED ORGANIC CARBON | Hydrophobic Organics (selectively adsorbed on non-ionic macroreticular resin) | Hydrophobic bases | One and two-ring aromatic amines except pyridine. |
| | | Hydrophobic acids | Aliphatic carboxylic acids of five to nine carbons, one and two-ring aromatic carboxylic acids, one and two-ring phenols, fulvic acid. |
| | | Hydrophobic neutrals | Hydrocarbons; aliphatic alcohols, amides, esters, ketones, and aldehydes > five carbons; aliphatic carboxylic acids and aliphatic amines > nine carbons; aromatic carboxylic acids and aromatic amines of three rings and greater. |
| | Hydrophilic Organics | Hydrophilic bases (adsorbed on strong acid, cation exchange resin) | Aliphatic amines ≤ nine carbons, amino acids, pyridine. |
| | | Hydrophilic acids (adsorbed on strong base anion exchange resin) | Aliphatic acids of ≤ five carbons, polyfunctional acids. |
| | | Hydrophilic neutrals (remains in solution) | Aliphatic amides, alcohols, aldehydes, esters, and ketones ≤ five carbons; polyfunctional alcohols; carbohydrates. |

FIGURE 1

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The hydrophilic acid, base and neutral fractions of the Leenheer scheme would contain the water extractable organics of particular interest to this task. The hydrophilic fractionation requires the specific conductance of the aqueous sample not to exceed 2000 μmhos/cm. At this concentration the inorganic ionic salts exceed the capacity of the ion-exchange resins, therefore dilution of the sample prior to fractionation would be required.

The overall methodology may be useful for initial screening of waste waters to determine the dissolved organic carbon (DOC) content in empirically defined categories present in water samples. However, if DOC measurement were the only analytical technique applied to the isolated fractions, the utility for environmental assessment programs would be limited. A DOC based scheme might be useful if before-and-after or upstream-downstream measurement of total organic content was of interest. For environmental assessment purposes it would be more useful to incorporate more specific analytical methods such as HPLC into the scheme. The severe limitation of the Leenheer _et al_ scheme for the analysis of water soluble organics in wastewaters is the low capacity of the ion exchange resins in the presence of inorganic ionic salts and the subsequent dilution of the sample prior to fractionation.

In another approach to organic analysis, Stalling _et al_ evaluated alkali metal hydroxides for their ability to retain, separate and enrich trace levels of acidic compounds in fish. The development of this technique was undertaken to recover phenols from Gel Permeation Chromatography (GPC) effluents of these samples. Ion exchange chromatography and base extraction procedures previously employed for the phenolic compounds and other weak acids recovered from water were found to be unsuccessful for the application to fish extracts and other complex chemical residues in aquatic ecosystems. Stalling's procedure uses Gel Permeation Chromatography to separate fatty acids from neutral and other acidic components. The enrichment of the phenols is achieved by insertion of small alkali metal hydroxide treated silica gel columns (1.0 cm i.d. x 2.0 cm) into the GPC effluent. The phenols are recovered by rinsing the column with 2 mL Methanol; the column can be reused after this wash. An extensive characterization of the formation of the alkali metal silica gels of Lithium, Cesium, Potassium and Sodium was undertaken. The physical and chromatographic properties of the various adsorbents were then characterized.

The Cs-silicate column was used for the retention of phenols from the effluent of the GPC system (mixture 1:1 v/v cyclohexane:methanol-methylene chloride gradient); the adsorbent retained acidic components in inverse order of $pK_a$ (i.e., most acidic species--lowest $pK_a$--were retained to the greatest extent).

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A comparison of the efficiency of the alkali-metal silica gel adsorbent to reverse phase HPLC for the separation of polar compounds demonstrated the superiority of the latter adsorbent. However, the reverse phase eluent (water/methanol) phase is not compatible with the GPC separation required for the complex sample extract matrices encountered by Stalling.

Stalling's procedure appears to be applicable to extracts containing hydrophilic materials, but not to aqueous solutions of water soluble organics. In the presence of water (pH <9) the metal cation incorporated in the resin is replaced with a proton. This severely restricts the application of the resins to the absorption of polar species from non-polar media.

A brief review of the Master Analytical Scheme (MAS) for the Analysis of Organic Compounds in water identified several areas of potential applicability to this program. The Master Analytical Scheme is a qualitative/quantitative scheme which includes organic compounds of those volatility classes and function group types which can be analyzed by Gas Chromatographic-Mass Spectrometry (GC/MS) directly or as derivatives.

The MAS uses the term "intractable" to describe non-purgeable, "non-extractable" organic materials. Compound identification in this exhaustive separation scheme is based on GC/MS analysis with computer searching of mass spectra data banks and manual interpretations. The intractable organic compounds are addressed as:

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Intractable volatile acids - Pentafluorobenzyl bromide (PFB) derivatization

Intractable non-volatile acids - Methylesters

Intractable secondary amines - Pentafluorobenzylbromide (PFB) derivatives

Intractable primary amines - Schiff bases of pentafluorobenzaldehyde

Neutral Intractables - Direct aqueous injection

The intractable model compounds used in the MAS study are listed in Table 1 and a summary of the analytical procedures for the separation and analysis are outlined in Table 2.

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## TABLE 1

### Intractable Model Compounds Used in MAS

| Physical/Chemical Property Class | Chemical Class | Compound |
|---|---|---|
| Strong Acids | Phosphoric/Phosphonic | Benzene phosphoric acid |
| | | Benzene phosphorous acid |
| | | Diphenyl phosphate |
| | | Dibutyl phosphite |
| | Sulfonic | Methane sulfonic acid |
| | | Benzene sulfonic acid |
| | | Toluene sulfonic acid |
| | | Naphthalene sulfonic acid |
| | | Chlorobenzene sulfonic acid |
| | Carboxylic | Acetic acid |
| | | Butyric acid |
| | | Crotonic acid |
| | | Hexanoic acid |
| | | Levulinic acid |
| | | Chloroacetic acid |
| | | Cyanoacetic acid |
| | | Dichloroacetic acid |
| | | 2-Bromo-*n*-butyric acid |
| | | Pyruvic acid |
| | | Methoxyacetic acid |
| | | Fuoric acid |
| | | Trichloroacetic acid |
| | | 3-Chloropropionic acid |
| | | Thioglycolic acid |
| | | Trimethylacetic acid |
| | | 2-Ethylhexanoic acid |
| | | Isobutyric acid |
| | | Formic acid |
| | | Trifluoroacetic acid |
| | | Bromoacetic acid |
| | | Thiolacetic acid |
| | | Maleic acid |
| | | Pentanoic acid |
| | | Hexanoic acid |
| | | Octanoic acid |
| | | Nonanoic acid |
| | | Oleic acid |
| Water Soluble Alcohols | Carbohydrates | Glucose |

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## TABLE 1 (Continued)

| Physical/Chemical Property Class | Chemical Class | Compound |
|---|---|---|
| Water Soluble Alcohols | Group I Alcohols | Glycerol |
| | | Methanol |
| | | Ethanol |
| | | 1-Propanol |
| | | 2-Propanol |
| | | 1-Butanol |
| | | 2-Butanol |
| | | 2-Chloroethanol |
| | | 1,3-Dihydroxyacetone |
| | | 3-Dimethylamino-1-propanol |
| | | 1-3-Dihydroxyacetone |
| | | 2-Aminopropanol |
| | | 2-Amino-2-methylpropanol |
| | | 2-Amino-2-methyl-1,3-propanediol |
| | | 2-Amino-2-(hydroxymethyl)1,3-propanediol |
| Basic Nitrogen Compounds | Alkyl/Aromatic Amines (1°,2°,3°) | Allylamine |
| | | *n*-Butylamine |
| | | Hexylamine |
| | | Benzylamine |
| | | Piperidine |
| | | Diallyamine |
| | | Morpholine |
| | | Di-*n*-butylamine |
| | | Triethylamine |
| | | Triallylamine |
| | | 3-Methoxypropylamine |
| | | Ethylene diamine |
| | | Pyrrolidine |
| | | Pyridine |
| | | Pyrazine |
| Polar Neutrals | Aldehydes | Propionaldehyde |
| | | *n*-Butyraldehyde |
| | | Crotonaldehyde |
| | | Heptaldehyde |
| | | Furfural |
| | | Valeraldehyde |
| | | Formaldehyde |
| | | Acetaldehyde |
| | | Acrolein |

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TABLE 1 (Continued)

| Physical Chemical Property Class | Chemical Class | Compound |
|---|---|---|
| Polar Neutrals | Ketones | Acetone |
| | | Methyl ethyl ketone |
| | | Cyclopentanone |
| | | Acetylacetone |
| | | 2-Heptanone |
| | | Cyclohexanone |
| Nonpolar Neutrals | Ester/Ethers | Methyl formate |
| | | Methyl acetate |
| | | Ethyl acetate |
| | | *t*-Butyl acetate |
| | | Propyl acetate |
| | | Allyl acetate |
| | | Ethyl butyrate |
| | | Tetrahydrofuran |
| | | 1,4-Dioxane |
| | Non-basic Nitrogen Compounds | Propionitrile |
| | | Acetonitrile |
| | | Acrylonitrile |
| | | Formamide |
| | | Nitromethane |
| | | Nitroethane |
| | | *t*-Nitrobutane |
| | | Benzonitrile |
| | | Acetamide |
| | | 1-Nitropropane |
| | | Dimethylacetamide |

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## TABLE 2

### Summary of the MAS for Intractable Organics

| Compound Category | Separation/Concentration | Analytical Method | Detection Limit | Other Comments |
|---|---|---|---|---|
| **Neutral Intractables** | - Addition of NaCl<br>- Fractional or azeotropic distillation | - Direct Aqueous Injection GC/MS | 100 µg/L | |
| Ionic Intractables<br>Volatile Carboxylic Acids | - Biorad AG 1-X8 Elute with solution of sodium bisulfate in $CH_3CN$: $H_2O$<br>- Distillation | - Derivatize with Pentafluorobenzyl bromide<br>- Concentration<br>- GC/MS | 10 ng total final vol. 0.3 mL | - Formic and Acetic Acid are procedural contaminants<br>- Chloride ion on the ion exchange resin will interfere with derivitization |
| Nonvolatile Acids | - Biorad AG 1-X10<br>- Elute with HCl/MeOH<br>- Solvent evaporation | - Derivatize with Diazomethane<br>- GC/MS | 10 ng | - Adsorption losses of methylated sulfonic and phosphonic acids during GC/MS<br>- Sample extracts deteriorate column performance<br>- Stability of derivatives unknown<br>- Interference from thermal decomposition of Humic Acids during GC. |
| Volatile Primary and<br>Secondary Amines | - Biorad AG 50W-X8<br>- Elute with NaOH in $CH_3CN$:$H_2O$<br>- Acidify eluant, evaporate to dryness, redissolve salts in base and extract with methyl-t-butyl ether | - Primary amines - derivatize one-half of extract with pentafluorobenzaldehyde<br>- Secondary amines - derivatize one-half of extract with pentafluorobenzyl bromide<br>- Concentration<br>- GC/MS | 10 ng total material | - Dimer of the secondary amine derivatizing reagent, pentafluorobenzyl bromide is an interference<br>- Storage stability of derivatives unknown. |

Recovery studies of the model compounds from several different water types was also conducted and reported. The ranges reported for the recovery of the model compounds were:

| Category | Matrix | Average % Recovery |
|---|---|---|
| Volatile Carboxylic Acids | Distilled water | 79 ± 9 |
| | Municipal effluent | 69 ± 11 |
| | Energy effluent | 76 ± 10 |
| Non-Volatile Acids | Spiked water samples | 66 ± 34 |
| Secondary Amines | Spiked Water samples | 43 ± 11 |
| Primary Amines | Spiked Water samples | 109 ± 44 |
| Neutral Intractables | Distilled water | 62 ± 9 |
| | Municipal effluent | 59 ± 11 |
| | Energy effluent | 66 ± 8 |

The MAS was conceived as a comprehensive analytical scheme predicated on the use of GC/MS/Computer. Because of the large number of specific sample handling and derivatization procedures included in the scheme, it would appear to be most useful for directed analysis of specific target compounds rather than as a survey analysis tool. The derivitization procedures included in the MAS would be valuable when specific confirmation/identification is required.

## 4 BACKGROUND

The scope of this task was to develop an extraction and analytical scheme for water soluble organics which is compatible with the goals of Level 1.

The major objective of Level 1 is to quantify mass emissions for organic classes. Although direct application of Level 1 methodology is not possible for "non-extractable organics, similar goals might be achieved by establishing a systematic classification scheme and appropriate analytical procedures. The residual unextracted water soluble organics indicated in Figure 2 illustrates the area of concern in this study.

The very volatile components present in the sample would be detected by Purge and Trap analysis. The extractable organics would be extracted and analyzed via the Level 1 analysis. The remaining extracted aqueous portion would then be analyzed for the water soluble organics.

In order to select the model compounds relevant to this program a practical definition of water soluble organics was established. The definition was established to direct the approach in the development of analytical procedures for the separation and detection of these compounds in water and waste water samples.

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"Water soluble organics" can be defined as "organics not purgeable or extractable with organic solvent." The extraction efficiency achievable by particular solvent extraction procedure is totally dependent on the tendency of the organic species in question to selectively partition into the organic solvent from water. The maximum achievable extraction efficiency

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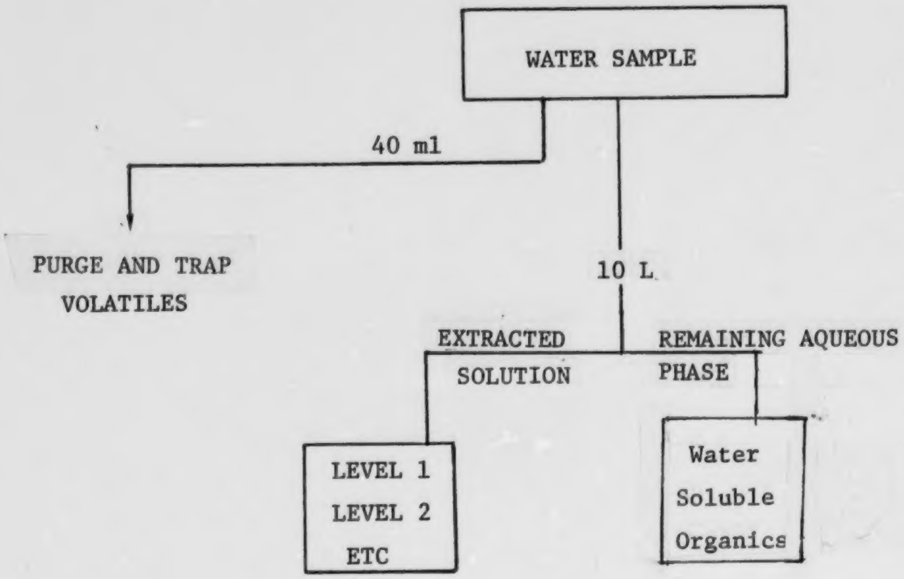
WATER SAMPLE
40 ml
PURGE AND TRAP VOLATILES
10 L.
EXTRACTED SOLUTION
REMAINING AQUEOUS PHASE
LEVEL 1
LEVEL 2
ETC
Water Soluble Organics

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Typing A

2

FIGURE 2

Illustration of the Comprehensive Analysis for Organics in Water

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for an organic compound in a given organic solvent/water system can be estimated if the partition coefficient for the compound in this system is known.

The partition coefficient, P, describes how a substance partitions between an aqueous and an organic phase under equilibrium conditions. Table 3 lists several organic compounds and their corresponding partition coefficients in three organic solvents of various polarities. For the inefficiently extracted compounds no one solvent shows a substantial affinity to preferentially extract these compounds from water more than another.

For a given compound/solvent system, the partition coefficient necessary to achieve 50% or 75% extraction recovery has theoretically been calculated to be 5 and 12 respectively (Appendix 1[11]). These partition coefficients have been calculated using the Level 1 solvent: sample ratios. The theoretical criteria used to predict extraction recoveries compare well with calculated and observed recoveries as listed in Table 4. This table illustrates several comparisons of actual and tabulated recoveries with the corresponding partition coefficients.

Using the above criteria, water soluble organics can be defined as those organic compounds having partition coefficients $\ll 5$; solvent extraction is not a viable method of separation of this category of compounds from water. With these restrictions the definition relates only to a relatively small number of organic compounds from several

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## TABLE 3[10]

### Illustrative Values of Solvent: Water Partition Coefficients

| Compound<br>Efficiently Extracted | $P_{CHCl_3:H_2O}$ | $P_{heptane:H_2O}$ | $P_{ether:H_2O}$ |
|---|---|---|---|
| Propyl ether | 580 | 34 | 18 |
| Hexyl amine | 490 | 30 | 16 |
| Butyl mercaptan | 1,200 | 98 | 34 |
| Benzene | 460 | 24 | 15 |
| Chlorobenzene | 6,200 | 1,100 | 150 |
| Indene | 78,000 | 1,500 | 180 |
| Acridine | 20,000 | 9,300 | 575 |
| Thiophene | 301 | 13 | 10 |
| **Inefficiently Extracted** | | | |
| Acetic Acid | 0.03 | 1.0 | 0.4 |
| Phenol | 2 | 0.005 | 31 |
| Benzene Sulfonic Acid | 0.0001 | 0.000006 | 0.002 |
| Ethylene glycol | 0.002 | 0.00001 | 0.005 |

## TABLE 4[12]

## Comparison of Calculated Recoveries with those Determined by Webb

| Compound | Extracted | Calculated | $P_{CHCl_3}$ |
|---|---|---|---|
| Naphthalene | 87 | 99 | 224 |
| o-Nitrotoluene | 91 | 76 | 21 |
| Benzothiazole | 96 | 100 | 560 |
| Phenol | 19 | 17 | 2 |
| p-Cresol | 50 | 60 | 12 |
| Dibenzofuran | 92 | 100 | 263,000 |

different organic classes of compounds that are truly water soluble organics. For example, 1-pentanol has a calculated $P_{CHCl_3}$ value of 10.0. This value corresponds to extraction recoveries in excess of 50% using organic solvents. 1-Pentanol would therefore not be considered as a water soluble organic compound in this study. For this method development effort the literature has been reviewed to identify those water soluble organic compounds which would be found most predominantly in the environment, therefore focusing on a slightly smaller number of water soluble organics.

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## 5. EXPERIMENTAL

### 5.A. EXPERIMENTAL APPROACH

Synthetic water samples containing the most common classes of water soluble organics were used to develop the techniques. In addition, a spiked sample and two real waste water samples were evaluated using the developed methodology.

The model compounds for this study were selected after reviewing the "United States Production and Sales, 1978 of Synthetic Chemicals"[13] and are listed in Table 5. Several of the compounds with the highest production and sales volume were evaluated in the likelihood that they might be the more common species in real wastewater samples. The tabulated values of octanol:water partition coefficients for the compounds listed in Table 5 show that these are indeed "non-extractable" species. The appropriate target concentrations for the analysis of these species ranged from low ppm (mg/L) to hundreds of ppm levels as deduced by examination of the Discharge Multimedia Environmental Goals (DMEG) levels for the individual compounds and categories, as specified in the EPA Multimedia Environmental Goals (MEG) study[14]. The DMEG values include reference criteria for organic concentration levels in water based on considerations of potential health and ecological effects.

The reported DMEG values (mg/L in water) for some of the water soluble organics such as butanol (DMEG 3200), ethylene glycol (DMEG 150) benzenesulfonic acid (DMEG 600) indicate that concentration, derivative formation, or ultra-sensitive detection devices are not necessary. Other water soluble organics may require concentration before analysis at the levels of interest.

5

## TABLE 5

### Water Soluble Organic Model Compounds

| Compound Category | Compound | Log $P_{oct}$ [15,16] |
|---|---|---|
| Acids | Citric | -1.72 |
| | Malonic | -0.73 |
| | Acetic | -0.17 |
| | Propionic | 0.33 |
| Alcohols | Methanol | -0.71 |
| | Ethanol | -0.31 |
| | Methoxy ethanol | -0.77 |
| | Isopropanol | 0.05 |
| | Butanol | 0.92 |
| Aldehydes | Formaldehyde | 0.096 |
| | Acetaldehyde | 0.52 |
| | Propionaldehyde | 1.2 |
| Amino Acids | L-Proline | |
| | β-Alanine | -2.83 |
| | DL-Methionine | -1.87 |
| Carbohydrates | Glucose | -3.24 |
| | Fructose | -3.01 |
| | Mannose | -3.24 |
| | Sucrose | -3.24 |
| Glycols | Sorbitol | -3.20 |
| | Glycerol | -2.87 |
| | Ethylene Glycol | -1.93 |
| | Propylene Glycol | -1.39 |
| | Diethylene Glycol | -1.94 |
| | Dipropylene Glycol | -1.13 |

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## TABLE 5 (Continued)

| Compound Category | Compound | Log $P_{oct}$ |
|---|---|---|
| Ketones | Acetone | -0.24 |
| | Methylethyl Ketone | 0.35 |
| | Cyclohexanone | 0.81 |
| | Mesityl Oxide | |
| Phenols | Resorcinol | 0.78 |
| | Phenol | 1.49 |
| | O-Cresol | 1.97 |
| Amines | Diethyl amine | 0.5 |
| | Monoethanolamine | |
| | Triethanolamine | -2.06 |
| | Dibutylamine | 1.44 |
| Sulfonic Acids | Linear Alkylbenzene Sulfonates | -2.26 |

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Typing Area

The approach taken for sample preparation and analysis of water soluble organics by direct aqueous injection is outlined in Table 6.

Direct aqueous injection liquid chromatography was explored as a mechanism to develop/identify retention time elution profiles to characterize compound classes. These elution profiles can be used to identify the category of an unknown water soluble organic and/or to reduce the number of possible compound categories it could belong to. This is achieved by analyzing the unknown samples under several standard chromatographic conditions to obtain the necessary retention time data. The retention times are then compared to the elution profiles for each compound category. A compound category is identified when the retention time data for a compound or unknown falls within the constraints of the elution profiles of one compound category for all of the standardized chromatographic conditions. This can be shown by the approach outlined below:

| Chromatographic Condition Compound Category | μ-C8 (RT min) | μC-18 (RT min) | μ-CN (RT min) |
|---|---|---|---|
| Alcohol, $\leq C_4$ | 5-10 | 10-20 | 3-5 |
| Glycols, $\leq C_4$ | <3 | 5-10 | <3 |
| Acids, $\leq C_4$ | 5-10 | 10-20 | 1-2 |

For example, water soluble alcohols and acids have similar retention times on the C8 and C18 HPLC systems, but different retention time windows in the μ-CN HPLC system.

In addition, the elution profiles can identify suitable methods for resolving individual compounds within each category.

## TABLE 6

## Sample Analysis of Water Soluble Organics by Direct Aqueous Injection

EXTRACTED AQUEOUS SAMPLE

|

(Purge Residual Solvent)

|

WATER + ORGANICS + SALTS

|

Analyze Organics by Direct Aqueous Injection,

HPLC, GC

## 5.B. EXPERIMENTAL DETAILS

This section of the report describes materials and instrumentation used and presents experimental details for the following direct aqueous injection (DAI) approach.

### 1. Materials

- Water Soluble Organic Model Compounds listed in Table 5 reagent grade
- Filters, Millipore type HA, 0.45 μm mixed cellulose acetate/ nitrate
- Acid 6N $H_2SO_4$ (Fisher)
- Waters, distilled, deionized water obtained from system such as Millipore MilliQ® System.
- Glassware:
  Syringes, 250 μL, 100 μL, 10 μL
  Volumetric flasks, sufficient to prepare calibration standards
  Volumetric pipettes
  Separatory funnels, 250 mLs, 1L
  Glass sparging device
- High Performance Liquid Chromatographic Columns:
  μ-Bondapak-C18, Waters Associates
  μ-Bondapak-Phenyl, Waters Associates
  μ-Bondapak E-125, Waters Associates
  Lichrosorb RP-2, Altex
- Gas Chromatographic column:
  Tenax GC 6' x 2 mm id glass, on column injection, Supelco

## 2. Instruments

- o High Performance Liquid Chromatographic System consisting of a Waters Associate U6K injector, 6000A pump, R-400 refractive index detector, Schoeffle variable UV detector.
- o Gas Chromatograph with Flame Ionization Detector, Hewlett Packard Model 5840, Varian Model 2700.
- o Analytical balance, Sauter type 404

## 3. Analytical Method - Direct Aqueous Injection (DAI)

The elution profiles for the DAI approach were constructed by chromatographing each of the water soluble model compounds on each of the five systems. These calibration solutions were prepared at several concentration levels in water, and injected directly into each of the systems described in Tables 7 and 8.

Environmental samples, spikes and blanks were screened on each of the five systems to evaluate the applicability of the DAI approach.

These samples were prepared for DAI analysis of the water soluble organics by adjusting the pH of each of the samples, spikes and blanks to $\leq 2$ with 6N $H_2SO_4$. The samples were then extracted with 3 x's 20 milliliters of methylene chloride. The remaining aqueous phase was then purged with nitrogen by means of a glass sparging tube for approximately ten minutes. The extracted aqueous samples were filtered through Millipore type HA 0.45 μm filters and then analyzed on each of the five chromatographic systems. The chromatographic analysis procedures are summarized in Tables 7 and 8.

## TABLE 7A

## HPLC Chromatographic Systems for Direct Aqueous Injection

| RP-2 | C18 |
|---|---|
| Column: LiChrosorb RP-2 | Column: μBondapak C18 |
| Flow, Mobile Phase: 1.5 mL $\min^{-1}$ $H_2O$ | Flow, Mobile Phase: 0.5 mL $\min^{-1}$ $H_2O$ |
| Detector: Refractive Index | Detector: Refractive Index |
| Attenuation: 8 x to 2 x (variable) | Attenuation: 2 x |
| Injection Volume: 10-200 μL (variable) | Injection Volume: 10 to 200 μL (variable) |

| E 125 | Phenyl |
|---|---|
| Column: μ-Bondapak E-125 | Column: μ-Bondapak Phenyl |
| Flow, Mobile Phase: 0.5 mL $\min^{-1}$ $H_2O$ | Flow, Mobile Phase: 1.5 mL $\min^{-1}$ $H_2O$ |
| Detector: Refractive Index | Detector: Refractive Index |
| Attenuation: 2 x | Attenuation: 2 x |
| Injection Volume: 10 - 200 μL (variable) | Injection Volume: 10 to 200 μL (variable) |

## TABLE 8

## GC/FID System for Direct Aqueous Injection

Gas Chromatography/Flame Ionization Detection System Tenax

Column: Tenax, 6' x 2 mm, glass

Conditions:

| | |
|---|---|
| Injector Temp | 275°C |
| Detector Temp | 300°C |
| Column Temp | programmed |
| Carrier Gas/Flow | Helium, 30 mLs/min |
| Air Flow | 300 mLs/min |
| Hydrogen Flow | 30 mLs/min |
| Chart Speed | 0.5 cm/min |
| Attenuation | $2^6 = 64$ |
| Injection Volume | 2 μL |

Column Temp Program:

| | |
|---|---|
| Initial Temp | 90°C |
| Initial Time | 1 minute |
| Final Temp | 280°C |
| Final Time | 5 minutes |
| Temp Increase Rate | 10°C/minute |

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## 6. RESULTS AND DISCUSSION

The DAI approach was investigated for its utility in providing qualitative and semi-quantitative data for the model water soluble organics. If the model compounds of one category showed sufficient differences in behaviors from compounds in another catgory under specific sets of chromatographic conditions, then elution profiles could be used to characterize an unknown mixture of compounds. To provide the information necessary for these profiles the model compounds selected were chromatographed on several HPLC systems with established chromatographic conditions.

The majority of the analytical techniques proposed in this program for the different organic classes involve High Performance Liquid Chromatography (HPLC). The use of reverse phase chromatography would allow direct aqueous injection (DAI) of relatively large volumes of water reducing the number of preparative steps involved in the analysis, but also reducing the detection limit. In addition DAI decreases the possibility of introducing extraneous material to an already complex matrix.

Retention times and precision and accuracy data for model compounds were determined and are reported in Table 9. The elution profile approach was tested with additional compounds and with an unknown sample. Quality control (QC) data for several of the water soluble organic model compounds were also obtained.

## 1. Elution Profiles

Elution profiles were produced by analyzing the model compounds on five chromatographic systems described in the experimental section. The HPLC systems used reverse phase columns, μC18 and RP-2, a phenyl bonded phase and a size-exclusion column. The GC system utilized a polyphenylether solid phase resin, Tenax-GC. Table 9 lists all the model compounds analyzed in each category and the retention time in minutes. The abbreviation designates the chromatographic systems used. These retention time data are visually illustrated in Figures 3 through 7. Each figure represents the elution profiles for the categories of water soluble organics chromatographed under each of the five conditions. The essence of the profile scheme lies in the distinct retention time data obtained for each category on the five systems. Positive identification of an unknown peak response is made by matching the retention times of the unknown species in each of the five systems with those of the categories. Conclusive evidence for a positive identification is supported when the five fold retention time data for one compound category match in each of the five chromatographic systems. Figures 8 through 16 illustrate the degree of separation within each category of water soluble model compounds under the five chromatographic conditions. These figures can be helpful in choosing the chromatographic column which will achieve the best separation between compounds within one compound category.

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# TABLE 9

## Retention Time Data for Model Compounds

| CATEGORY | COMPOUND | RP-2 Retention Time (min) | E-125 Retention Time (min) | C18 Retention Time (min) | Phenyl Retention Time (min) | Tenax Retention Time (min) |
|---|---|---|---|---|---|---|
| **Acids** | Citric | 1.7 | 6.0 | - a. | 2.0 | - a. |
| | Malonic | 1.8 | 6.2 | - | 2.1 | - |
| | Acetic | 2.4 | 6.7 | - | 2.3 | - |
| | Propionic | 3.1 | 7.5 | - | 3.6 | - |
| **Alcohols** | Methanol | 2.5 | 6.4 | 7.5 | 2.4 | 1.2 |
| | Ethanol | 2.9 | 6.7 | 10.7 | 2.8 | 2.6 |
| | Methoxyethanol | 3.2 | 6.6 | 14.8 | 3.2 | 7.4 |
| | Isopropanol | 3.4 | 7.0 | 19.7 | 3.6 | 4.0 |
| | Butanol | 6.1 | 8.7 | ND | 7.8 | 7.4 |
| **Aldehydes** | | | | | | |
| | Formaldehyde | 2.1 | 6.2 | 6.4 | 2.1 | 1.2 |
| | Acetaldehyde | 2.9 | 7.0 | ND | 2.8 | 1.8 |
| | Propionaldehyde | 4.1 | 7.8 | ND | ND | 4.1 |
| **Amino Acids** | L-Proline | 2.3 | 6.2 | 7.2 | 2.2 | ND |
| | β-Alanine | 2.3 | 6.0 | 6.0 | 2.6 | ND |
| | DL-Methionine | 2.3 | 6.3 | 9.7 | 2.6 | ND |
| **Carbohydrates** | | | | | | |
| | Glucose | 2.0 | 6.0 | 6.1 | 2.0 | ND |
| | Fructose | 2.0 | 6.0 | 6.2 | 2.2 | ND |
| | Mannose | 2.0 | 6.1 | 6.2 | 2.0 | ND |
| | Sucrose | 2.0 | 6.0 | 7.9 | 2.1 | ND |
| **Glycols** | Sorbitol | 2.0 | 5.8 | 6.2 | 2.0 | 8.4 |
| | Glycerol | 2.1 | 6.2 | 6.6 | 2.1 | 13.7 |
| | Ethylene glycol | 2.2 | 6.1 | 7.1 | 2.2 | 7.4 |
| | Propylene glycol | 2.4 | 6.4 | 9.3 | 2.5 | 8.3 |
| | Diethylene glycol | 2.8 | 6.4 | 14.5 | 3.0 | 13.7 |
| | Dipropylene glycol | 4.7 | 7.2 | ND | 6.8 | 13.7 |

## TABLE 9 (Continued)

| CATEGORY | COMPOUND | RP-2 Retention Time (min) | E-125 Retention Time (min) | C18 Retention Time (min) | Phenyl Retention Time (min) | Tenax Retention Time (min) |
|---|---|---|---|---|---|---|
| Ketones | Acetone | 4.5 | 7.7 | ND | 4.6 | 4.3 |
| | Methyl ethyl ketone | 6.8 | 8.7 | ND | 8.7 | 6.7 |
| | Cyclohexanone | 14.5 | 11.1 | ND | 24.2 | 13.4 |
| | Mesityl oxide | 23.0 | 14.6 | ND | ND | 11.3 |
| Phenols | Resorcinol | 4.5 | 14.1 | ND | 7.0 | 16.7 |
| | Phenol | 7.0 | 14.3 | ND | 11.6 | 12.2 |
| | o-Cresol | 14.5 | 21.1 | ND | 30.6 | 13.3 |
| Amines | Diethylamine | ND | ND | ND | ND | ND |
| | Monoethanolamine | ND | ND | ND | ND | ND |
| | Triethanolamine | 2.3 | 6.5 | 6.5 | 2.1 | ND |
| | Dibutylamine | ND | ND | ND | ND | 11.5 |

a. Chromatographed poorly with non-reproducible retention times

N.D. Not detected at the highest concentration level tested.

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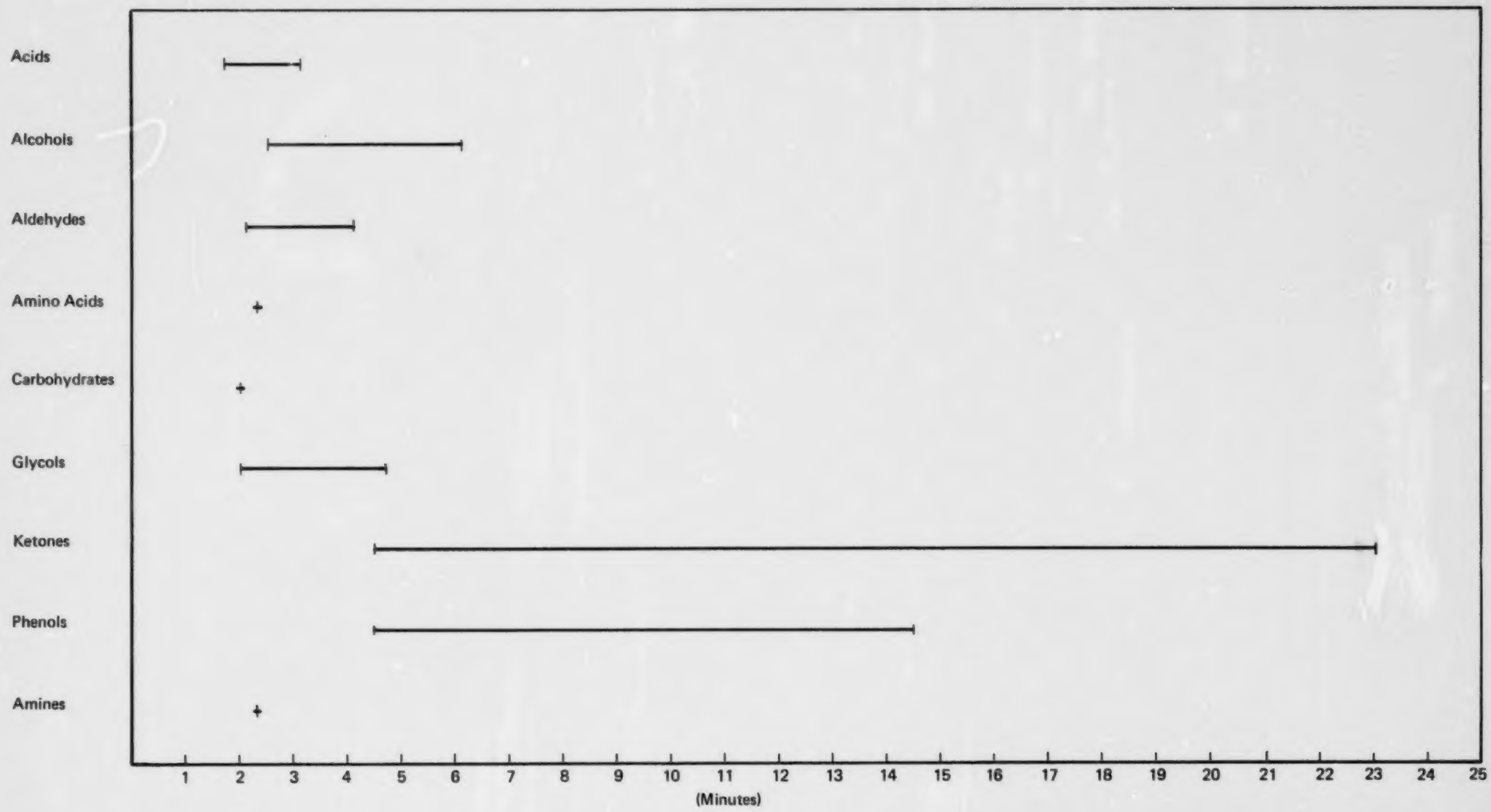

3 Elution Profile

FIGURE 3: Elution Profile System RP-2

HKJ RP-2

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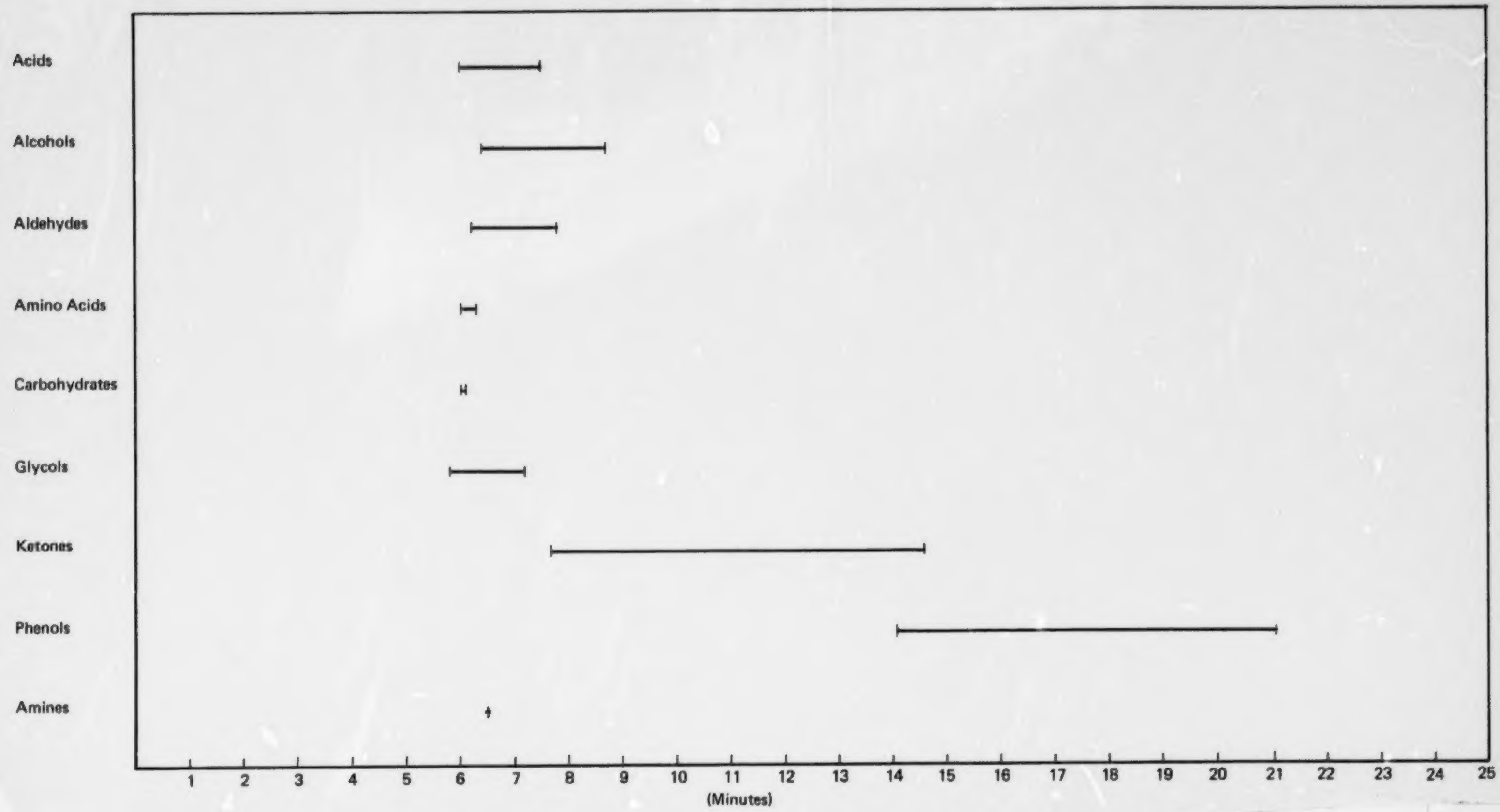

Elution Profile

FIGURE 4: Elution Profile System E-125

8 ~~#4~~ E-125

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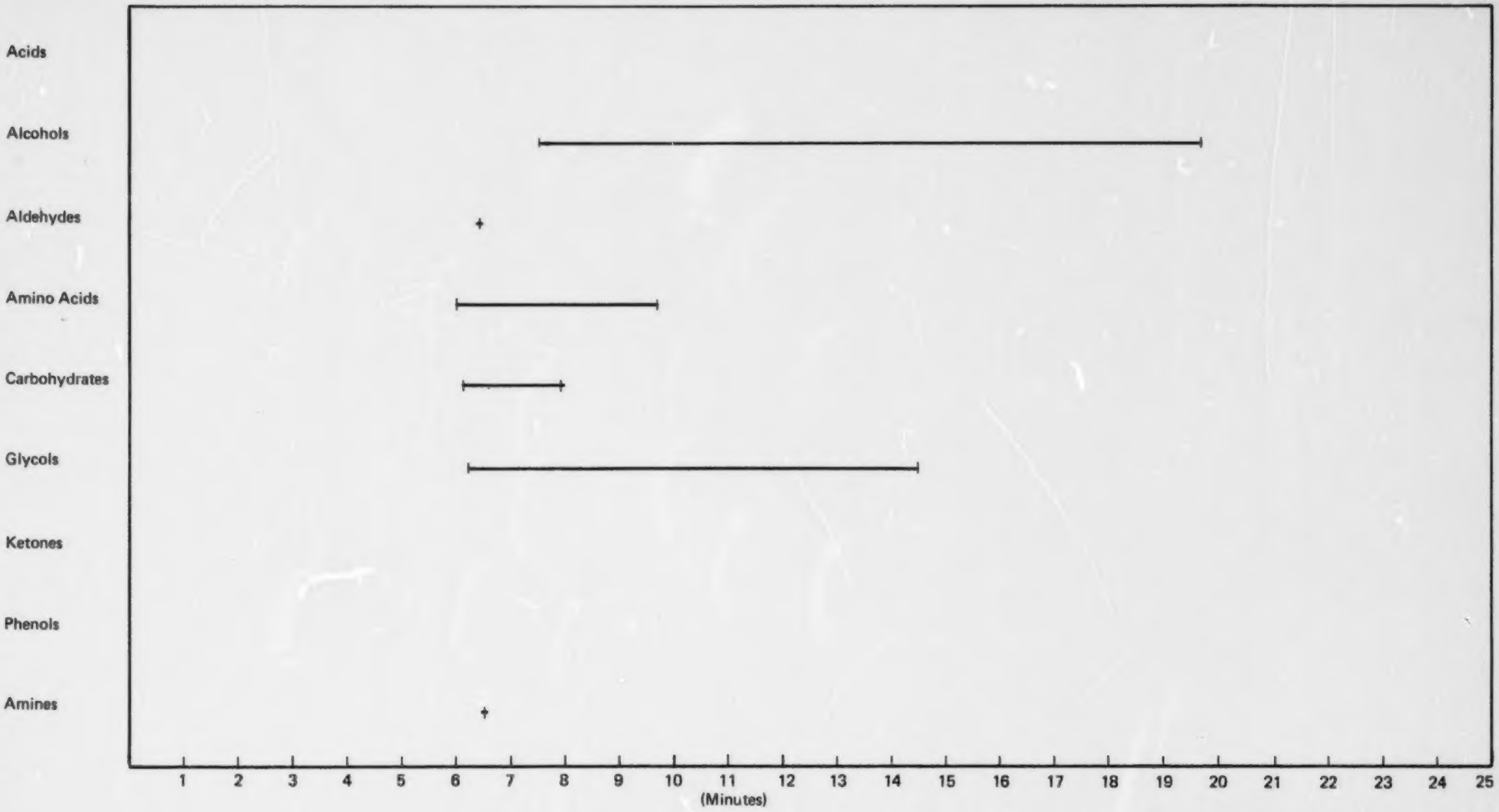

Elution Profile

FIGURE 5: Elution Profile System C18

~~VI3~~ 5 C18

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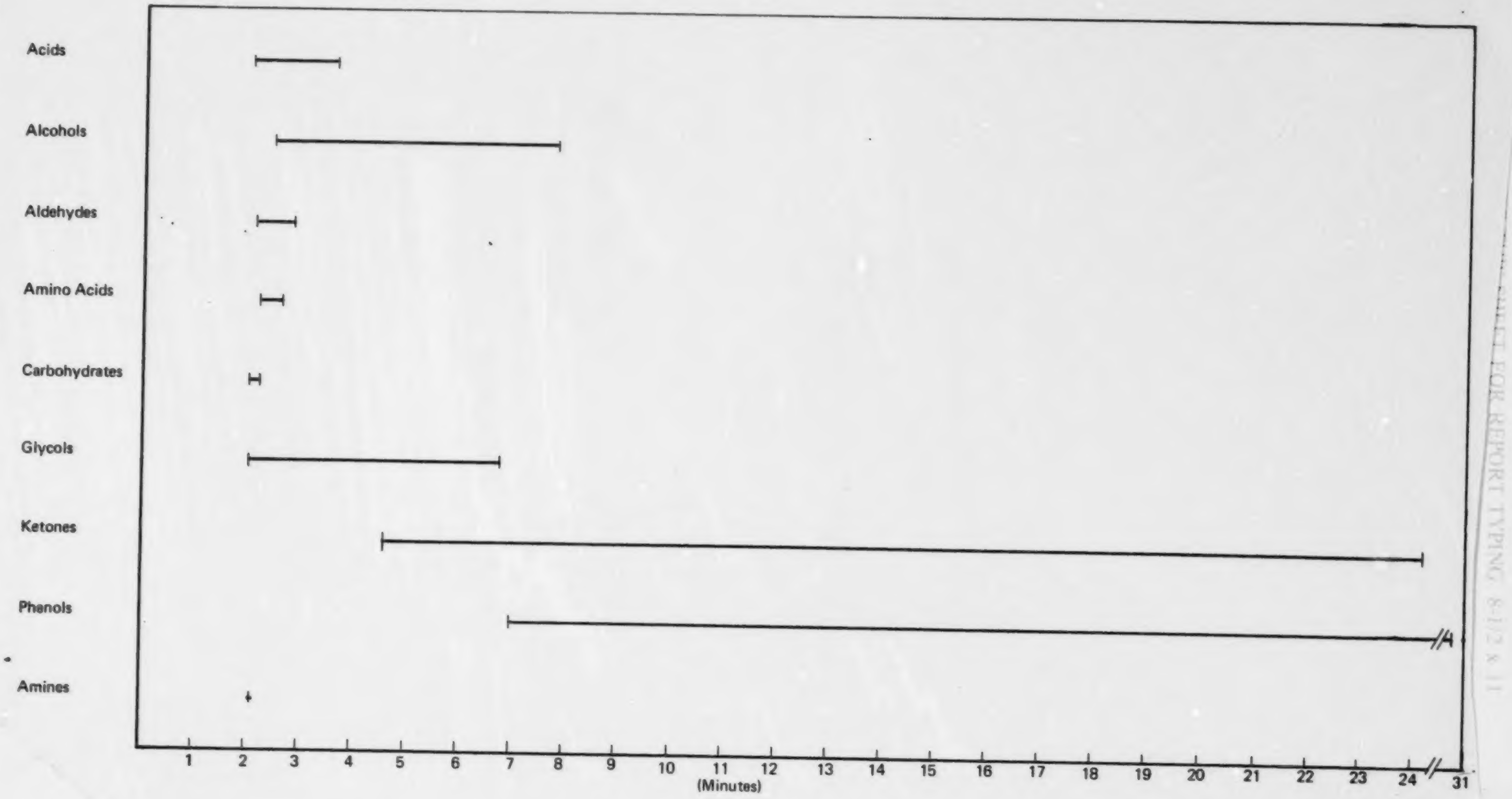

Elution Profile

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scale

FIGURE 6: Elution Profile System Phenyl

6 - VI-4 Phenyl

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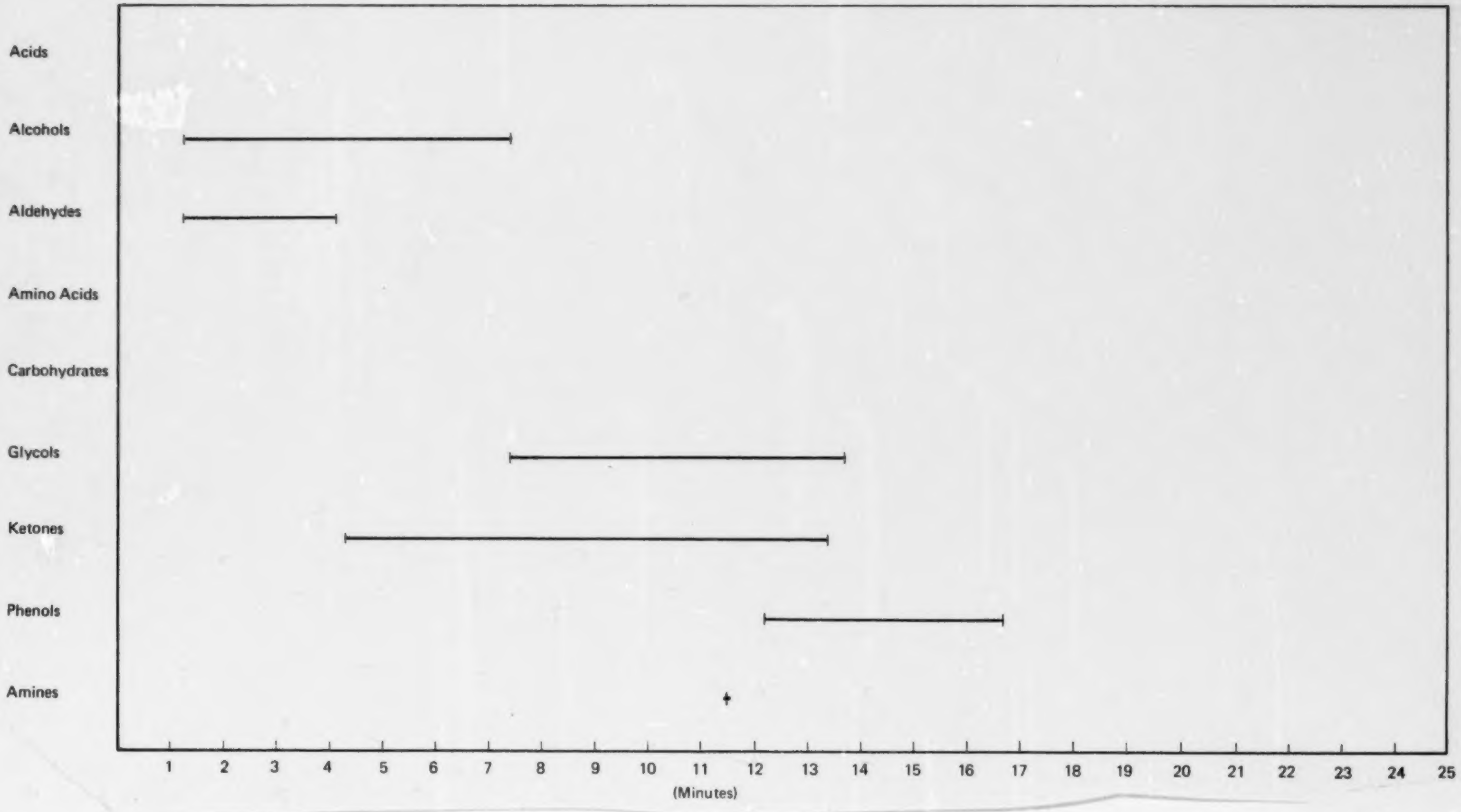

Elution Profile

FIGURE 7: Elution Profile System Tenax

7 ~~VA~~ Tenax

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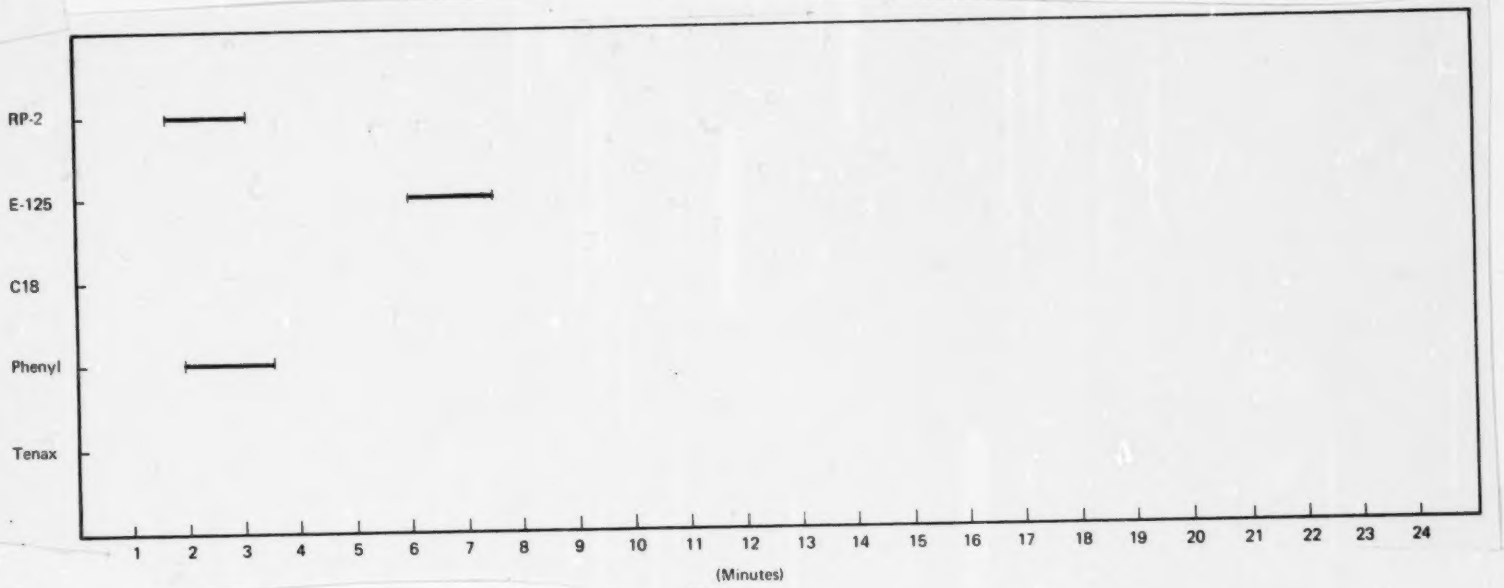


FIGURE 8: Elution Profile for Acids

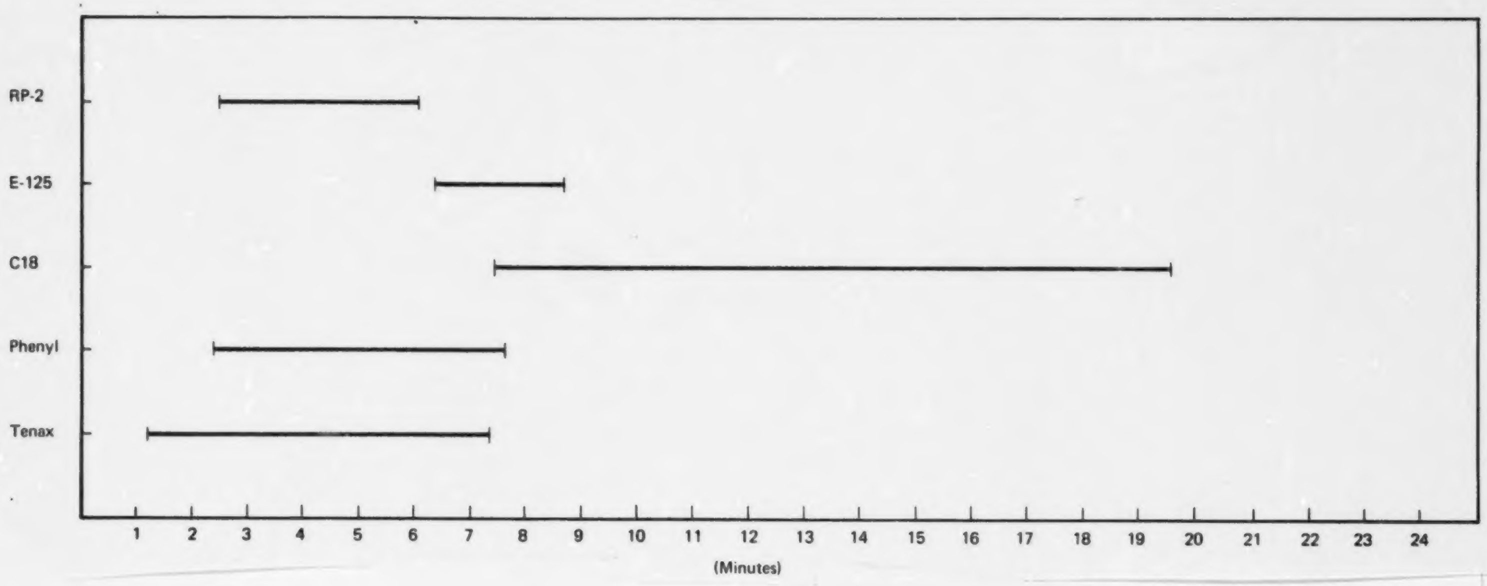


FIGURE 9: Elution Profile for Alcohols

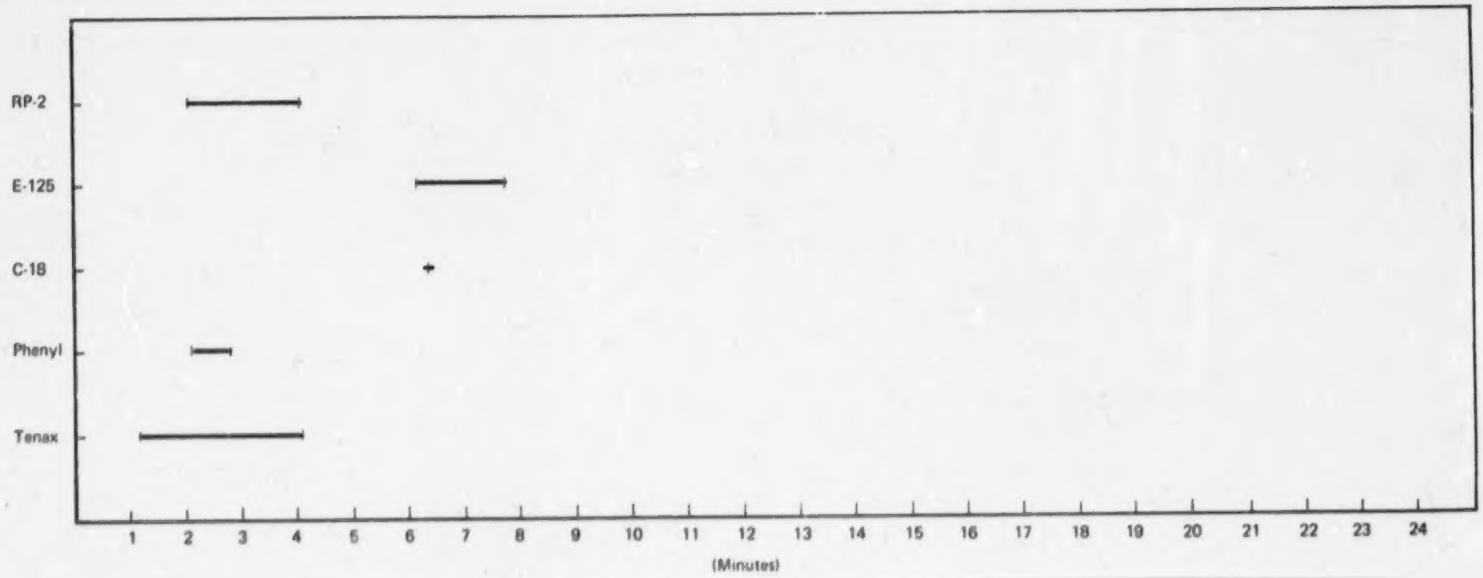


FIGURE 10: Elution Profile for Aldehydes

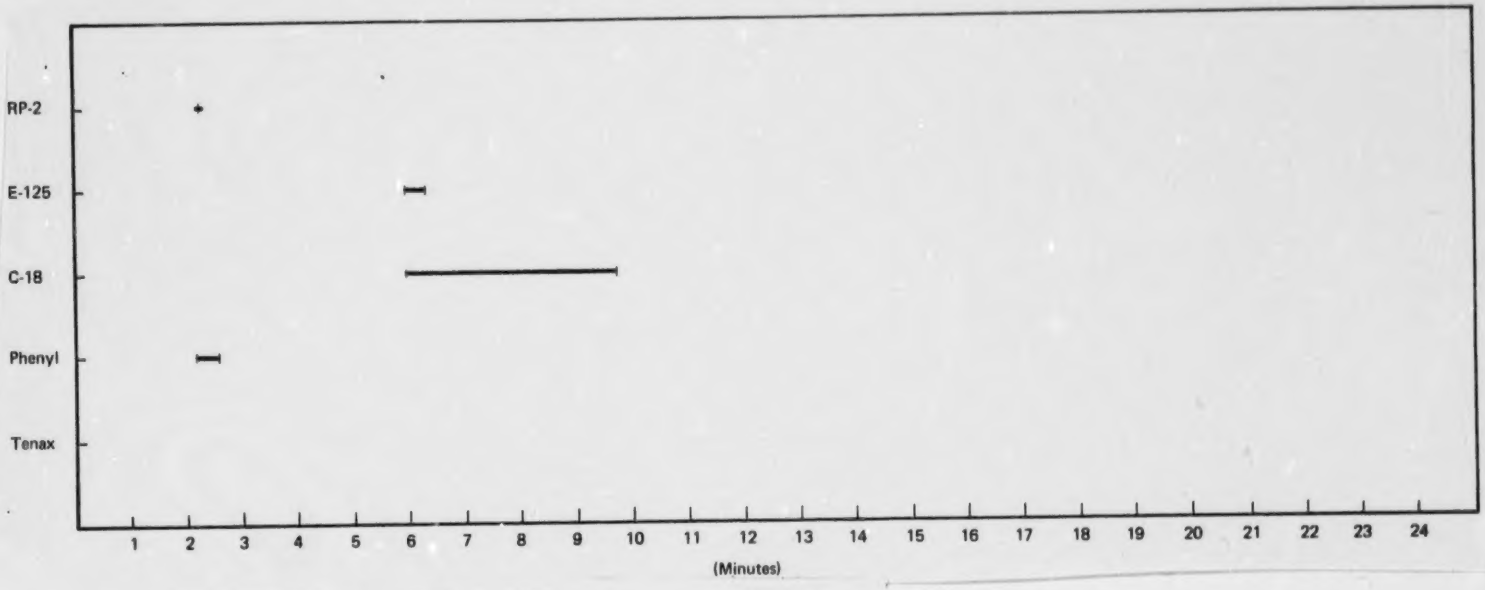
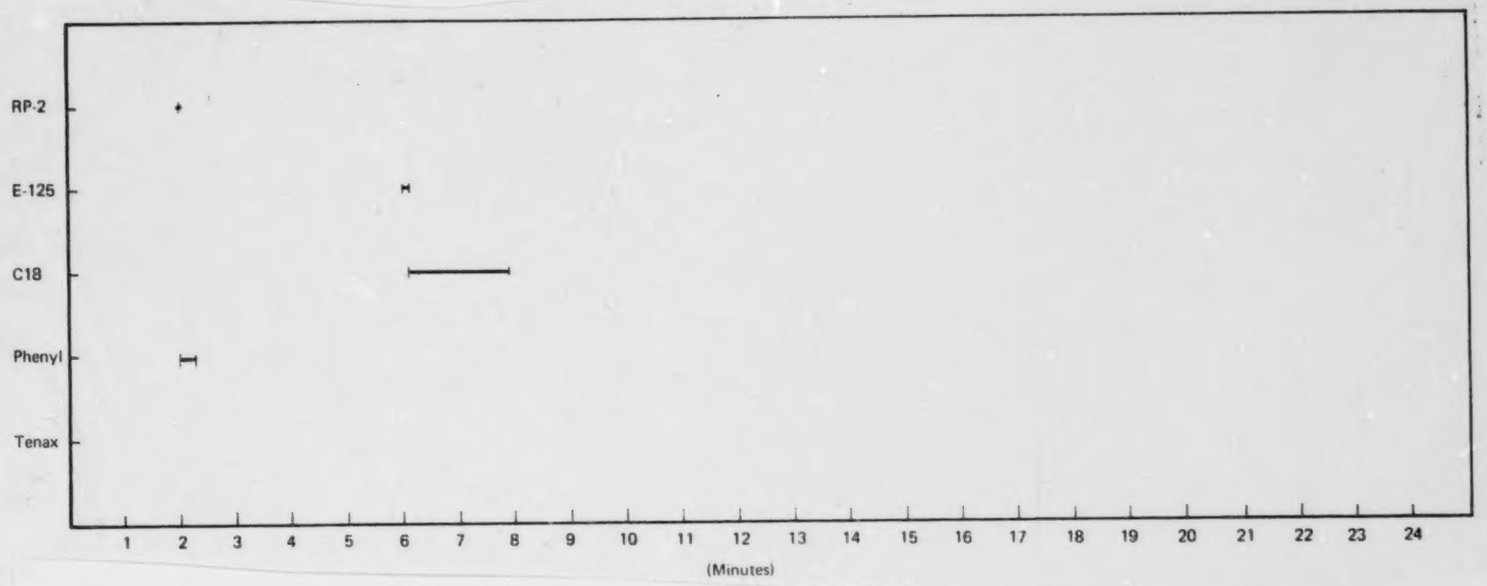
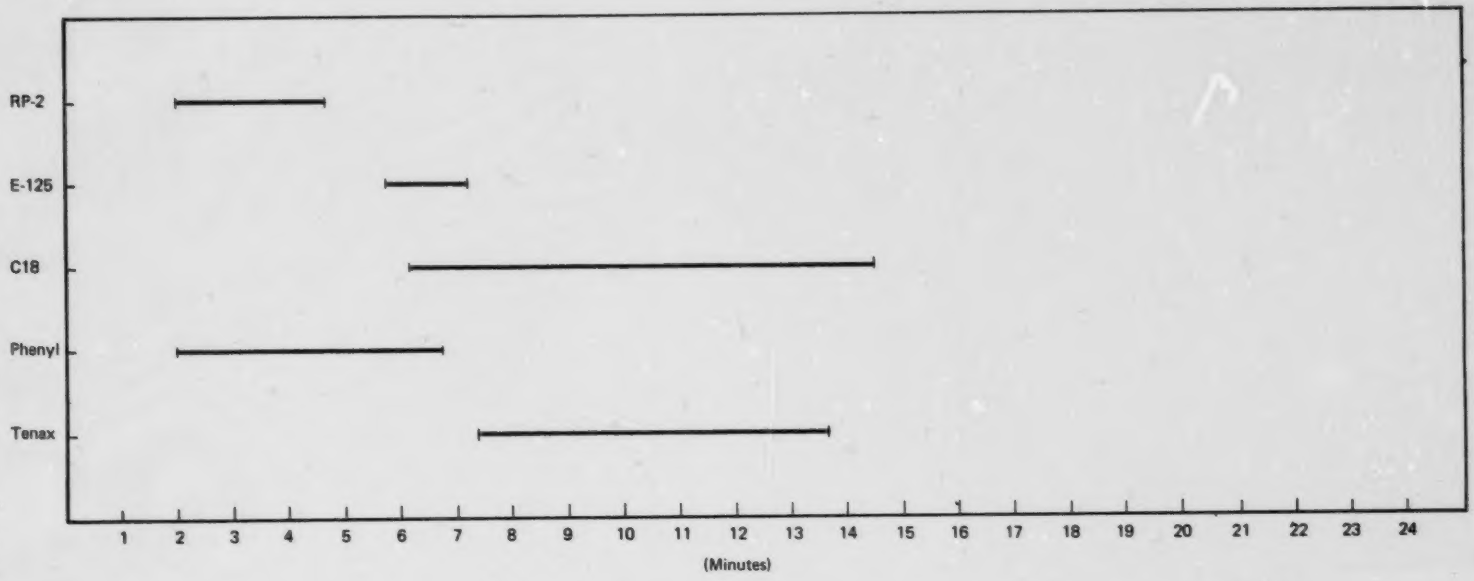


Figure 11: Elution Profile for Amino Acids



Elution Profile for

FIGURE 12: Elution Profile for Carbohydrates



Elution Profile for

FIGURE 13: Elution Profile for Glycols

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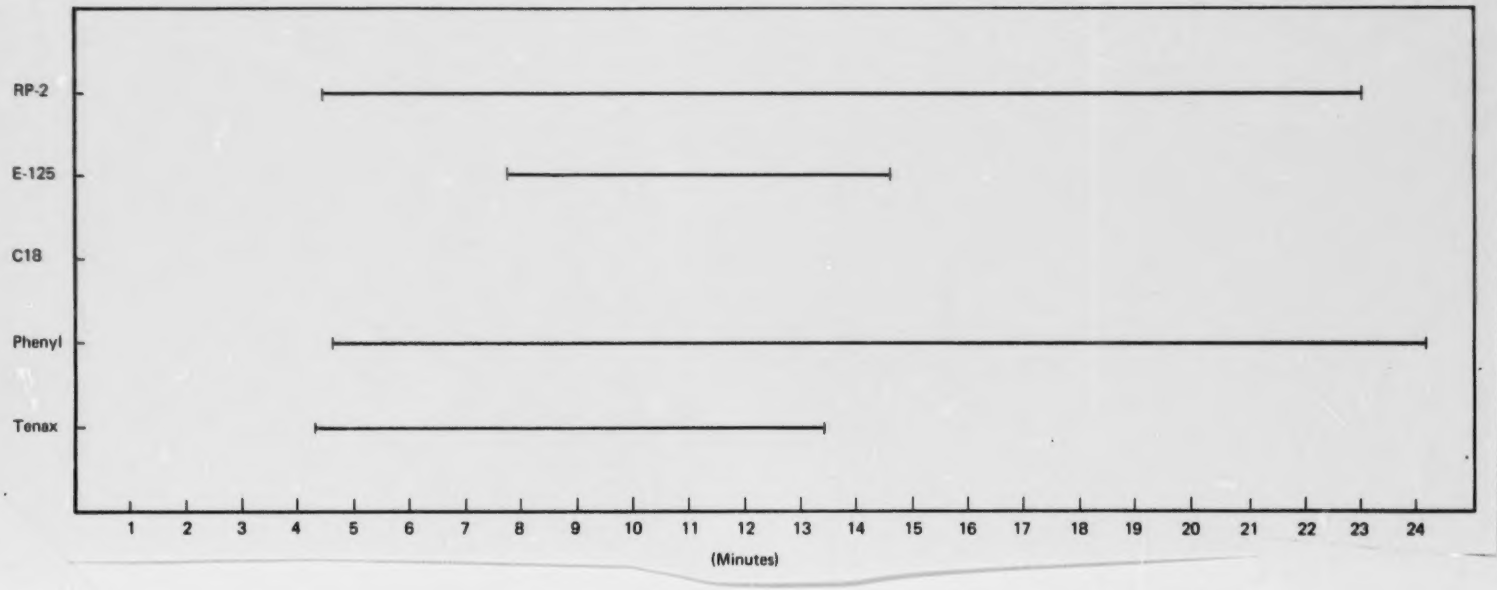

Elution Profile for

FIGURE 14: Elution Profile for Ketones

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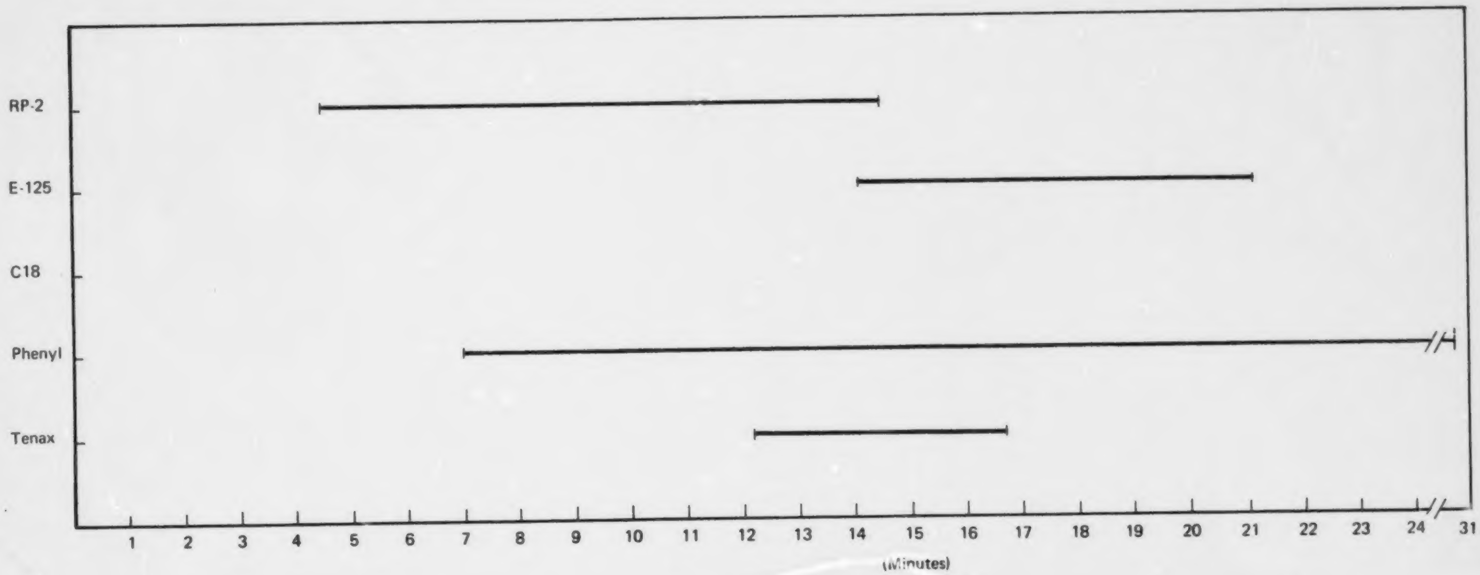

FIGURE 15: Elution Profile for Phenols

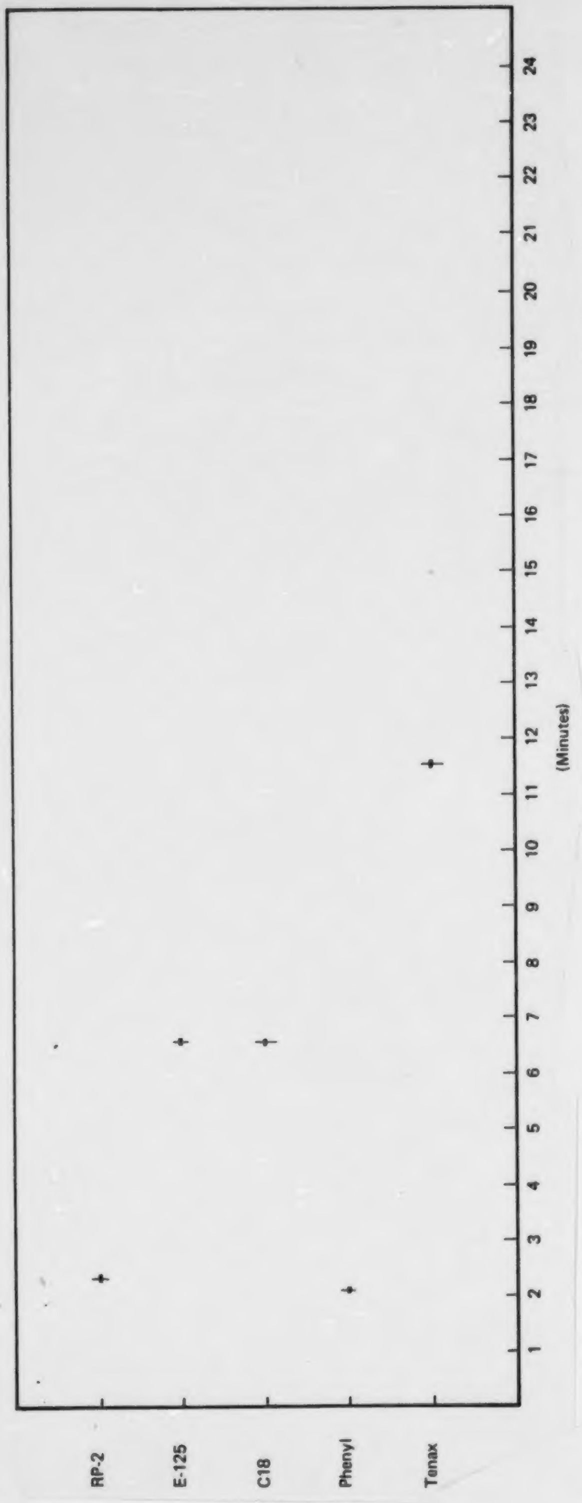

Figure 16: Elution Profile for Amines

To determine the precision and accuracy of the methods, calibration mixtures of each compound category were chromatographed. The precision for most of the systems is defined by a correlation coefficient greater than 0.998. Table 10 lists the concentrations for all calibration standards. Four concentration levels of each category were prepared and analyzed separately. Tables 11 through 15 list the linear regression data and detection limits for the model compounds on each of the five systems.

A plot of concentration versus peak height or concentration versus area was used to produce the linear regression data. The sum of the concentrations and of total peak area was used when no separation occurred between several compounds with a category. Detection limits reported are defined as three times the baseline noise. The calibration data for L-Proline and Propionic Acid are plotted in calibration curves in Figures 17 and 18 to illustrate the range of precisions obtained for the different systems.

## TABLE 10

10

### Concentration Data for Model Compounds

| COMPOUND | CAL 1 mg/L | CAL 2 mg/L | CAL 3 mg/L | CAL 4 mg/L |
|---|---|---|---|---|
| **Acids** | | | | |
| Citric | 204.7 | 102.4 | 61.4 | 20.5 |
| Malonic | 204.4 | 102.2 | 61.3 | 20.4 |
| Acetic | 274.0 | 137.0 | 82.2 | 27.4 |
| Propionic | 198.6 | 99.3 | 59.6 | 19.9 |
| **Alcohols** | | | | |
| Methanol | 158.2 | 79.1 | 47.5 | 15.8 |
| Ethanol | 157.8 | 78.9 | 47.3 | 15.8 |
| Methoxyethanol | 193.0 | 96.5 | 57.9 | 19.3 |
| Isopropanol | 157.2 | 78.6 | 47.2 | 15.7 |
| Butanol | 162.0 | 81.0 | 48.6 | 16.2 |
| **Aldehydes** | | | | |
| Formaldehyde | 224.4 | 122.2 | 67.3 | 22.4 |
| Acetaldehyde | 156.6 | 78.3 | 47.0 | 15.7 |
| Propionaldehyde | 161.2 | 80.6 | 48.4 | 16.1 |
| **Amino Acids** | | | | |
| L-Proline | 214.0 | 107.0 | 64.2 | 21.4 |
| β-Alanine | 251.2 | 125.6 | 75.4 | 25.1 |
| DL-Methionine | 205.2 | 102.6 | 61.6 | 20.5 |
| **Carbohydrates** | | | | |
| Glucose | 205.0 | 102.5 | 61.5 | 20.5 |
| Fructose | 214.6 | 107.3 | 64.4 | 21.5 |
| Mannose | 205.4 | 102.7 | 61.6 | 20.5 |
| Sucrose | 184.4 | 92.2 | 55.3 | 18.4 |

~~VI-2~~ 10

TABLE 10 (Continued)

Concentration Data for Model Compounds

| COMPOUND | CAL 1 mg/L | CAL 2 mg/L | CAL 3 mg/L | CAL 4 mg/L |
|---|---|---|---|---|
| Glycols | | | | |
| Sorbitol | 197.4 | 98.7 | 59.2 | 19.7 |
| Glycerol | 209.2 | 104.6 | 62.8 | 20.9 |
| Ethylene Glycol | 177.4 | 88.7 | 53.2 | 17.7 |
| Propylene Glycol | 183.2 | 91.6 | 55.0 | 18.3 |
| Diethylene Glycol | 163.2 | 81.6 | 49.0 | 16.3 |
| Dipropylene Glycol | 179.8 | 89.9 | 53.9 | 18.0 |
| Ketones | | | | |
| Acetone | 157.8 | 78.9 | 47.3 | 15.8 |
| Methyl ethyl ketone | 161.0 | 80.5 | 48.3 | 16.1 |
| Cyclohexanone | 189.6 | 94.8 | 56.9 | 19.0 |
| Mesityl oxide | 288.8 | 144.4 | 86.6 | 28.9 |
| Phenols | | | | |
| Resorcinol | 357.0 | 178.5 | 107.1 | 35.7 |
| Phenol | 217.8 | 108.9 | 65.3 | 21.8 |
| o-Cresol | 200.0 | 100.0 | 60.0 | 20.0 |
| Amines | | | | |
| Diethylamine | 141.2 | 70.6 | 42.4 | 14.1 |
| Monoethanolamine | 203.6 | 101.8 | 61.1 | 20.4 |
| Triethanolamine | 199.4 | 99.7 | 59.8 | 19.9 |
| Dibutylamine | 153.4 | 76.7 | 46.0 | 15.3 |

## TABLE 11

Chromatographic System RP-2

| Compound | Retention Time (min) | Linear Regression Data b | m | cc | Detection Limit (ppm) |
|---|---|---|---|---|---|
| **Acids** | | | | | |
| Citric | 1.7 | -21.9 | 0.416 | 0.993 | 20 |
| Malonic | 1.8 | | | | |
| Acetic | 2.4 | 3.29 | 0.362 | 0.999 | 10 |
| Propionic | 3.1 | 8.28 | 0.251 | 0.988 | 5 |
| **Alcohols** | | | | | |
| Methanol | 2.5 | 0.167 | 0.0983 | 0.996 | 40 |
| Ethanol | 2.9 | -1.44 | 0.302 | 0.998 | 20 |
| Methoxyethanol | 3.2 | -1.06 | 0.435 | 0.999 | 20 |
| Isopropanol | 3.4 | -2.56 | 0.518 | 0.999 | 20 |
| Butanol | 6.1 | 0.0223 | 0.161 | 0.999 | 25 |
| **Aldehydes** | | | | | |
| Formaldehyde | 2.1 | 0.0760 | 0.269 | 0.999 | 20 |
| Acetaldehyde | 2.9 | -0.209 | 0.077 | 0.999 | 30 |
| Propionaldehyde | 4.1 | -0.7891 | 0.0358 | 0.999 | 80 |
| **Amino Acids** | | | | | |
| L-Proline | 2.3 | -3.15 | 0.147 | 0.997 | 15 |
| B-Alanine | | | | | |
| DL-Methionine | | | | | |
| **Carbohydrates** | | | | | |
| Glucose | 2.0 | 0.684 | 0.199 | 0.999 | 10 |
| Fructose | | | | | |
| Mannose | | | | | |
| Sucrose | | | | | |

11

TABLE 11 (Continued)

| Compound | Retention Time (min) | Linear Regression Data b | m | cc | Detection Limit (ppm) |
|---|---|---|---|---|---|
| **Glycols** | | | | | |
| Sorbitol | 2.0 | -1.136 | 0.199 | 0.999 | 20 |
| Glycerol | 2.1 | | | | |
| Ethylene Glycol | 2.2 | | | | |
| Propylene Glycol | 2.4 | | | | |
| Diethylene Glycol | 2.8 | -0.062 | 0.332 | 0.999 | 10 |
| Dipropylene Glycol | 4.7 | -0.500 | 0.110 | 1.000 | 20 |
| **Ketones** | | | | | |
| Acetone | 4.5 | 0.324 | 0.155 | 0.999 | 30 |
| Methyl ethyl ketone | 6.8 | 0.894 | 0.087 | 0.996 | 50 |
| Mesityl oxide | 23.0 | | | | >250 |
| Cyclohexanone | 14.5 | -1.00 | 0.053 | 1.000 | 100 |
| **Phenols** | | | | | |
| Phenol | 7.0 | 1.659 | 0.174 | 0.998 | 20 |
| Resorcinol | 4.5 | 0.849 | 0.058 | 0.999 | 20 |
| o-Cresol | 14.5 | 1.478 | 0.331 | 0.999 | 20 |
| **Amines** | | | | | |
| Diethylamine | ND | | | | >150 |
| Monoethanolamine | ND | | | | >200 |
| Triethanolamine | 2.3 | | | | 100 |
| Dibutylamine | ND | | | | >150 |

ND = not detected at highest concentration standard.

TABLE 12

12

Chromatographic System E-125

| Compound | Retention Time (min) | Linear Regression Data |  |  | Detection Limit (ppm) |
|---|---|---|---|---|---|
|  |  | b | m | cc |  |
| **Acids** |  |  |  |  |  |
| Citric | 6.0 | 2.70 | 133.8 | 0.998 | 20 |
| Malonic | 6.2 |  |  |  |  |
| Acetic | 6.7 | 2.05 | 0.757 | 0.999 | 10 |
| Propionic | 7.5 | 6.39 | 0.892 | 0.995 | 10 |
| **Alcohols** |  |  |  |  |  |
| Methanol | 6.4 | -0.55 | 0.302 | 1.00 | 15 |
| Ethanol | 6.7 |  |  |  |  |
| Methoxyethanol | 6.6 |  |  |  |  |
| Isopropanol | 7.0 | -2.18 | 0.616 | 0.999 | 10 |
| Butanol | 8.7 | -2.31 | 0.407 | 0.999 | 20 |
| **Aldehydes** |  |  |  |  |  |
| Formaldehyde | 6.2 | 11.4 | 0.873 | 0.995 | 5 |
| Acetaldehyde | 7.0 |  |  |  | >160 |
| Propionaldehyde | 7.8 |  |  |  | >160 |
| **Amino Acids** |  |  |  |  |  |
| L-Proline | 6.2 | -177.3 | 132.5 | 0.999 | 10 |
| β-Alanine | 6.0 |  |  |  |  |
| DL-Methionine | 6.3 |  |  |  |  |
| **Carbohydrates** |  |  |  |  |  |
| Glucose | 6.0 | 1670.6 | 80.5 | 0.999 | 5 |
| Fructose | 6.0 |  |  |  |  |
| Mannose | 6.1 |  |  |  |  |
| Sucrose | 6.0 |  |  |  |  |

## TABLE 12 (Continued)

| Compound | Retention Time (min) | Linear Regression Data b | m | cc | Detection Limit (ppm) |
|---|---|---|---|---|---|
| **Glycols** | | | | | |
| Sorbitol | 5.8 | 3.73 | 0.323 | 0.999 | 5 |
| Glycerol | 6.2 | | | | |
| Ethylene Glycol | 6.1 | 0.564 | 0.554 | 1.00 | 10 |
| Propylene Glycol | 6.4 | | | | |
| Diethylene Glycol | 6.4 | 0.270 | 0.314 | 0.999 | 10 |
| Dipropylene Glycol | 7.2 | | | | |
| **Ketones** | | | | | |
| Acetone | 7.7 | 1.22 | 0.695 | 0.999 | 10 |
| Methyl ethyl ketone | 8.7 | -7.36 | 0.583 | 0.998 | 25 |
| Mesityl oxide | 14.6 | -5.80 | 0.264 | 0.998 | 30 |
| Cyclohexanone | 11.1 | -5.79 | 0.655 | 0.999 | 25 |
| **Phenols** | | | | | |
| Phenol | 14.3 | 0.994 | 0.243 | 0.999 | 15 |
| Resorcinol | 14.1 | | | | |
| o-Cresol | 21.1 | -0.114 | 0.237 | 0.999 | 20 |
| **Amines** | | | | | |
| Diethylamine | ND | | | | >150 |
| Monoethanolamine | ND | | | | >200 |
| Triethanolamine | 6.5 | 0.745 | 0.0939 | 0.922 | 50 |
| Dibutylamine | ND | | | | >150 |

ND = Not detected at highest concentration standard.

## TABLE 13

13

Chromatographic System C18

| Compound | Retention Time (min) | Linear Regression Data b | m | cc | Detection Limit (ppm) |
|---|---|---|---|---|---|
| **Acids** | | | | | |
| Citric | a. | | | | |
| Malonic | | | | | |
| Acetic | | | | | |
| Propionic | | | | | |
| **Alcohols** | | | | | |
| Methanol | 7.5 | 0.769 | 0.0974 | 0.996 | 40 |
| Ethanol | 10.7 | 0.948 | 0.204 | 0.997 | 25 |
| Methoxyethanol | 14.8 | 0.159 | 0.179 | 0.998 | 20 |
| Isopropanol | 19.7 | 0.237 | 0.130 | 0.998 | 30 |
| Butanol | ND | | | | >200 |
| **Aldehydes** | | | | | |
| Formaldehyde | 6.4 | -0.842 | 0.482 | 0.999 | 10 |
| Acetaldehyde | ND | | | | >200 |
| Propionaldehyde | ND | | | | >200 |
| **Amino Acids** | | | | | |
| L-Proline | 7.2 | -2.58 | 0.531 | 1.000 | 15 |
| β-Alanine | 6.0 | -3.22 | 0.647 | 0.999 | 15 |
| DL-Methionine | 9.7 | -0.258 | 0.403 | 0.999 | 15 |
| **Carbohydrates** | | | | | |
| Glucose | 6.1 | 1.09 | 0.214 | 0.999 | 5 |
| Fructose | 6.2 | | | | |
| Mannose | 6.2 | | | | |
| Sucrose | 7.9 | 0.597 | 0.216 | 0.999 | 5 |

## TABLE 13 (Continued)

| Compound | Retention Time (min) | Linear Regression Data b | m | cc | Detection Limit (ppm) |
|---|---|---|---|---|---|
| **Glycols** | | | | | |
| Sorbitol | 6.2 | -0.0726 | 0.593 | 0.999 | 10 |
| Glycerol | 6.6 | -0.212 | 0.456 | 0.999 | 10 |
| Ethylene Glycol | 7.1 | -0.575 | 0.362 | 0.999 | 15 |
| Propylene Glycol | 9.3 | 0.172 | 0.266 | 0.999 | 15 |
| Diethylene Glycol | 14.5 | -2.05 | 0.151 | 0.998 | 40 |
| Dipropylene Glycol | ND | | | | >200 |
| **Ketones** | | | | | |
| Acetone | ND | | | | >150 |
| Methyl ethyl ketone | ND | | | | >150 |
| Mesityl oxide | ND | | | | >200 |
| Cyclohexanone | ND | | | | >300 |
| **Phenols** | | | | | |
| Phenol | ND | | | | >200 |
| Resorcinol | ND | | | | >200 |
| o-Cresol | ND | | | | >200 |
| **Amines** | | | | | |
| Diethylamine | ND | | | | >150 |
| Monoethanolamine | ND | | | | >200 |
| Triethanolamine | 6.5 | 1.54 | 0.0591 | 0.997 | 60 |
| Dibutylamine | ND | | | | >150 |

They look [illegible]

a. Chromatographed poorly, non-reproducible retention times.

## TABLE 14

Chromatographic System Phenyl

| Compound | Retention Time (min) | Linear Regression Data b | Linear Regression Data m | Linear Regression Data cc | Detection Limit (ppm) |
|---|---|---|---|---|---|
| Acids | | | | | |
| Citric | 2.0 | 4.50 | 0.330 | 1.00 | 10 |
| Malonic | 2.1 | | | | |
| Acetic | 2.3 | -3.63 | 0.407 | 0.999 | 20 |
| Propionic | 2.6 | 4.17 | 0.286 | 0.999 | 20 |
| Alcohols | | | | | |
| Methanol | 2.4 | -0.538 | 0.122 | 0.991 | 25 |
| Ethanol | 2.8 | -0.162 | 0.270 | 0.998 | 20 |
| Methoxyethanol | 3.2 | 16.8 | 0.253 | 0.983 | 25 |
| Isopropanol | 3.6 | 1.26 | 0.251 | 0.999 | 15 |
| Butanol | 7.8 | -1.51 | 0.0962 | 0.999 | 50 |
| Aldehydes | | | | | |
| Formaldehyde | 2.1 | 1.06 | 0.441 | 0.999 | 10 |
| Acetaldehyde | 2.8 | -1.56 | 0.0661 | 0.989 | 75 |
| Propionaldehyde | ND | | | | >160 |
| Amino Acids | | | | | |
| L-Proline | 2.2 | 0.581 | 0.519 | 0.999 | 10 |
| β-Alanine | 2.6 | 0.255 | 0.265 | 0.995 | 10 |
| DL-Methionine | 2.6 | | | | |
| Carbohydrates | | | | | |
| Glucose | 2.0 | 2.29 | 0.177 | 1.00 | 15 |
| Fructose | 2.2 | | | | |
| Mannose | 2.0 | | | | |
| Sucrose | 2.1 | | | | |

TABLE 14 (Continued)

| Compound | Retention Time (min) | Linear Regression Data b | m | cc | Detection Limit (ppm) |
|---|---|---|---|---|---|
| **Glycols** | | | | | |
| Sorbitol | 2.0 | | | | |
| Glycerol | 2.1 | 2.92 | 0.376 | 1.00 | 10 |
| Ethylene Glycol | 2.2 | | | | |
| Propylene Glycol | 2.5 | 1.42 | 0.551 | 0.999 | 10 |
| Diethylene Glycol | 3.0 | 1.99 | 0.428 | 0.999 | 10 |
| Dipropylene Glycol | 6.8 | 0.809 | 0.176 | 1.000 | 30 |
| **Ketones** | | | | | |
| Acetone | 4.6 | -1.35 | 0.201 | 0.999 | 50 |
| Methyl ethyl ketone | 8.7 | -0.628 | 0.0824 | 0.996 | 80 |
| Mesityl oxide | ND | | | | >300 |
| Cyclohexanone | 24.2 | -0.103 | 0.0374 | 0.999 | 150 |
| **Phenols** | | | | | |
| Phenol | 11.6 | 2.18 | 0.175 | 0.999 | 10 |
| Resorcinol | 7.0 | 1.77 | 0.372 | 0.999 | 20 |
| o-Cresol | 30.6 | 1.29 | 0.462 | 0.999 | 50 |
| **Amines** | | | | | |
| Diethylamine | ND | | | | >150 |
| Monoethanolamine | ND | | | | >200 |
| Triethanolamine | 2.1 | 2.08 | 0.338 | 0.992 | 60 |
| Dibutylamine | ND | | | | >150 |

## TABLE 15 /5

Chromatographic System Tenax

| Compound | Retention Time (min) | Linear Regression Data b | Linear Regression Data m | Linear Regression Data cc | Detection Limit (ppm) |
|---|---|---|---|---|---|
| **Acids** | | | | | |
| Citric | ND [a] | | | | >210 |
| Malonic | ND | | | | >210 |
| Acetic | ND | | | | >280 |
| Propionic | ND | | | | >200 |
| **Alcohols** | | | | | |
| Methanol | 1.2 | 1.16 | 0.854 | 0.986 | 3 |
| Ethanol | 2.6 | -4599.3 | 503.1 | 0.999 | 4 |
| Methoxyethanol | 7.4 | 435.4 | 460.8 | 0.999 | 4 |
| Isopropanol | 4.0 | -3362.1 | 569.6 | 0.999 | 9 |
| Butanol | 7.4 | | | | 4 |
| **Aldehydes** | | | | | |
| Formaldehyde | 1.2 | -819.9 | 149.2 | 0.998 | 6 |
| Acetaldehyde | 1.8 | -1813.5 | 383.7 | 0.999 | 4 |
| Propionaldehyde | 4.1 | -2575.1 | 439.1 | 0.999 | 5 |
| **Amino Acids** | | | | | |
| L-Proline | ND | | | | >250 |
| β-Alanine | ND | | | | >250 |
| DL-Methionine | ND | | | | >250 |
| **Carbohydrates** | | | | | |
| Glucose | ND [b] | | | | >250 |
| Fructose | ND | | | | >500 |
| Mannose | ND | | | | >250 |
| Sucrose | ND | | | | >500 |

## TABLE 15 (Continued)

| Compound | Retention Time (min) | Linear Regression Data b | m | cc | Detection Limit (ppm) |
|---|---|---|---|---|---|
| **Glycols** | | | | | |
| Sorbitol | 8.4 | | | | >200 |
| Glycerol | 13.7 | | | | >200 |
| Ethylene Glycol | 7.4 | | | | >200 |
| Propylene Glycol | 8.3 | | | | >200 |
| Diethylene Glycol | 13.7 | | | | >200 |
| Dipropylene Glycol | 13.7 | | | | >200 |
| **Ketones** | | | | | |
| Acetone | 4.3 | -2648.8 | 539.9 | 0.999 | 4 |
| Methyl ethyl ketone | 6.7 | -2871.3 | 639.2 | 0.999 | 4 |
| Mesityl oxide | 11.3 | -2507.1 | 404.9 | 1.00 | 4 |
| Cyclohexanone | 13.4 | 0.236 | 0.0724 | 0.999 | 5 |
| **Phenols** | | | | | |
| Phenol | 12.2 | -10239.5 | 867.7 | 0.999 | 4 |
| Resorcinol | 16.7 | -4.35 | 0.0438 | 0.996 | 25 |
| o-Cresol | 13.3 | -5523.0 | 836.8 | 0.999 | 3 |
| **Amines** | | | | | |
| Diethylamine | ND | | | | >150 |
| Monoethanolamine | ND | | | | >200 |
| Triethanolamine | ND | | | | >200 |
| Dibutylamine | 11.5 | | | | >150 |

a. Peaks detected for citric, acetic and propionic acid at 1000 ppm, however, chromatographed poorly and did not exhibit reproducible retention times.

b. Peaks detected for fructose and sucrose (12.2 and 13.9 min respectively) at 1000 ppm level.

ND= Not detected at highest concentration standard.

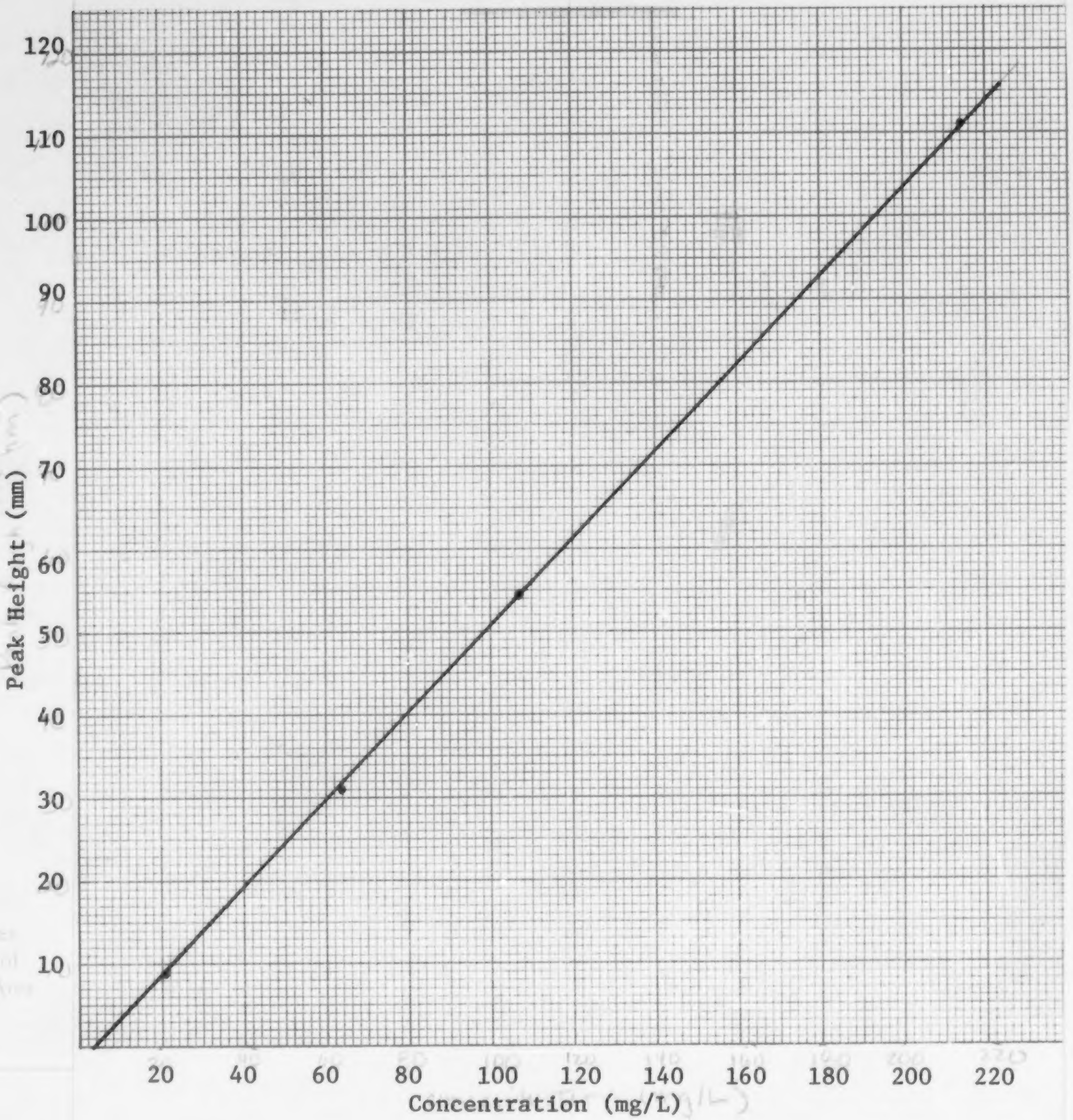

FIGURE 17

L-Proline Calibration Curve

Conditions: Chromatographic System C18

10 Lines to End of Typing Area

For Page Numbering

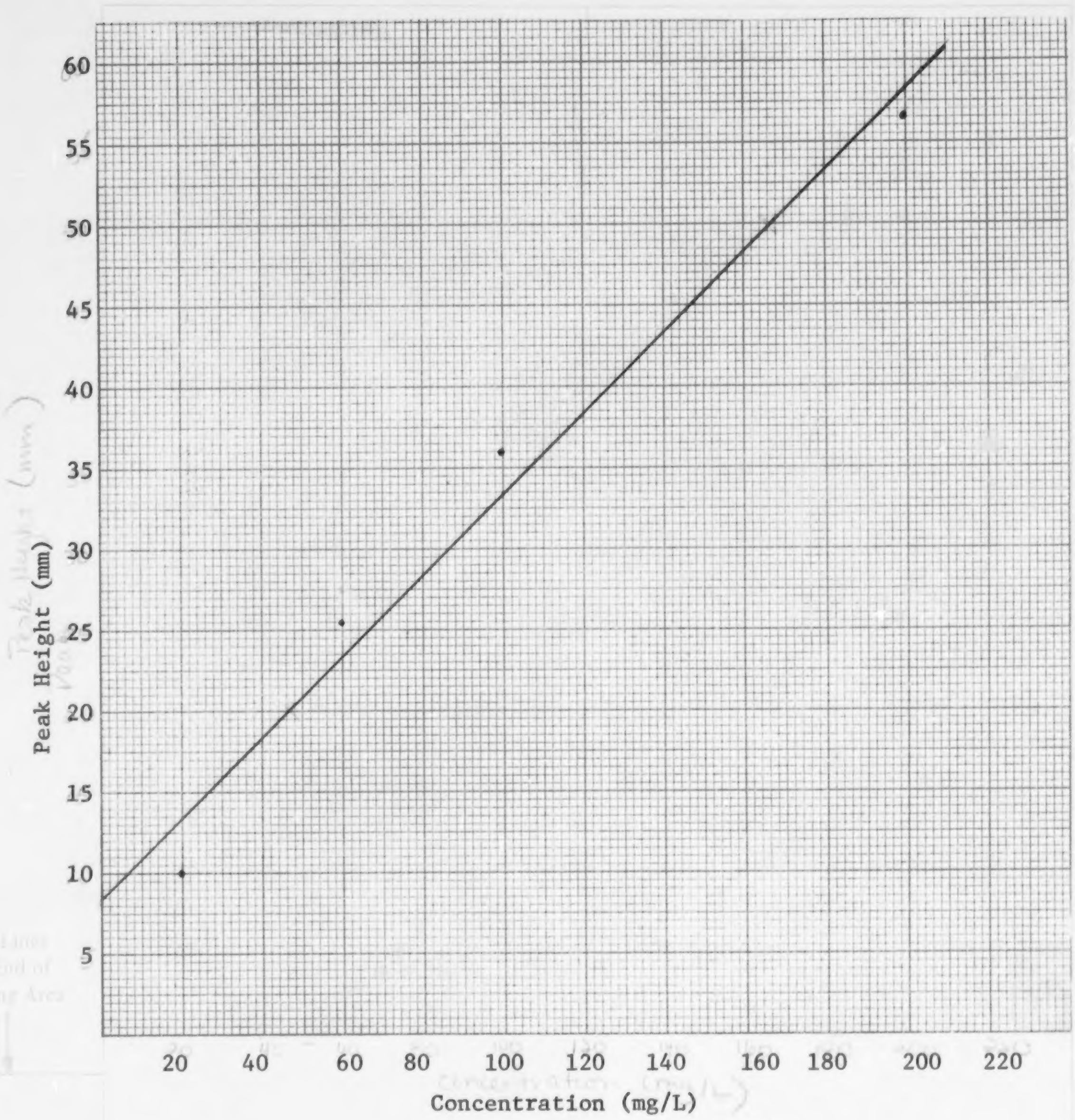

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FIGURE 18

Propionic Acid Calibration Curve

Conditions: Chromatographic System RP-2

## 2. DAI of Test Mixture

The elution profiles can be used to identify and/or screen mixtures of unknown components. To test the elution profile scheme, a spiked water sample containing water soluble organics (other than the model compounds used for method development) was evaluated on the five chromatographic systems. The objective of this experiment was to determine if compounds other than the tested model compounds could be identified as to the category in which they belong by the elution profile scheme. The test mixture contained the following concentrations of compounds spiked into Milli-Q water:

10 Lines to End of Typing Area

| | |
|---|---|
| Acetonitrile | 157.1 ppm |
| t-Butanol | 161.9 ppm |
| 2-Butanone | 161.1 ppm |
| Triethylamine | 145.5 ppm |

The mixture was analyzed under the five chromatographic conditions to obtain retention time data for all detected species. The retention time data are listed in Table 16. The chromatographic conditions were identical to those used to determine the compound class retention windows. Under these conditions, all the components could not be baseline resolved.

Evaluation of these retention time data provides the following information: A maximum of four components appear to exist as detected in Chromatographic Systems Phenyl and Tenax. Therefore, one might expect to identify up to four compound categories as possibly present in this mixture.

There are several possible approaches for comparison of the retention time data with the elution profiles. One approach is to compare the retention time data generated on each chromatographic system with the corresponding elution profile (Figure 3 to 7) for that system, and to identify all possible compound categories that might be associated with each peak observed on that system. For example, Figure 3 indicates that the peak with a retention time of 3.5 minutes on System RP-2 might be due to a water soluble alcohol, aldehyde or glycol. Table 17 illustrates the results of such a comparison for the four component synthetic test mixture. Examination of this table shows only two categories of compounds--alcohols and ketones--for which there is a consistent pattern for all five

## TABLE 16

### Retention Time Data for Test Mixture

| System: | Retention Time (min)/Peak Height*(mm) | | | | |
|---|---|---|---|---|---|
| | RP-2 | E-12 | C18 | Phenyl | Tenax |
| | | | | 3.3/29 | |
| | | | | 3.4/29 | 3.4/98000* |
| | 3.6/29 | | | | |
| | 4.1/48 | | | | |
| | | | | | 4.6/122000* |
| | | | | 4.85/31 | |
| | | | | | 5.9/91000* |
| | 7.0/12.5 | | | | |
| | | 7.5/182 | | | |
| | | | | | 7.8/11 |
| | | 9.25/35 | | | |
| | | | | 9.4/5.5 | |
| | | | 12.4/42 | | |
| | | | 12.8/20 | | |

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*Peak Area (arbitrary units)

3

10 Lines
to End of
Typing Area

17

## TABLE 17

### Compound Categories Indicated by Elution Profiles

| | System RP-2 | | | System E-125 | | System C18 | | System Phenyl | | | | System Tenax | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | (Ret.Time-min.) | | | (Ret.Time-min) | | (Ret.Time-min) | | (Ret.Time-min) | | | | (Ret.Time-min) | | | |
| | 3.5 | 4.1 | 7.0 | 7.5 | 9.25 | 12.4 | 12.8 | 3.3 | 3.4 | 4.85 | 9.4 | 3.4 | 4.6 | 5.9 | 7.8 |
| Acids | | | | ✓ | | | | ✓ | ✓ | | | ✓ | ✓ | ✓ | |
| Alcohols | ✓ | ✓ | | ✓ | | ✓ | ✓ | ✓ | ✓ | ✓ | | ✓ | | | |
| Aldehydes | ✓ | ✓ | | ✓ | | | | | | | | | | | |
| Amino Acids | | | | | | | | | | | | | | | |
| Carbohydrates | | | | | | | | | | | | | | | |
| Glycols | ✓ | ✓ | | | | ✓ | ✓ | ✓ | ✓ | ✓ | | | | | ✓ |
| Ketones | | | ✓ | | ✓ | a | | | | ✓ | ✓ | | ✓ | ✓ | ✓ |
| Phenols | | | ✓ | | | | | | | | ✓ | | | | |
| Amines | | | | | | | | | | | | | | | |

---

a Ketones are not detected below ∿200 ppm under System C18.

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chromatographic systems; there is at least one peak within the correct retention time window on each system for these two categories. Water soluble alcohols and ketones could be tentatively identified as present and, in fact, t-butanol and t-butanone are components of the test mixture. Other categories of water soluble organics, for example carboxylic acids, can be ruled out because there are no peaks in the appropriate retention windows for all the systems. Similarly, there is no evidence to indicate the presence of water soluble carbohydrates, since there are no peaks in the carbohydrate retention time region on any of the systems.

An alternative approach for generating essentially the same information is to use a clear plastic guide sheet, ruled as shown in Figure 19, and to mark on it the retention times for each peak observed in the unknown sample. Figure 20 illustrates what the grid would look like for the data in Table 16. The clear plastic version of Figure 20 can be used as an overlay on the elution profiles of Figures 8 to 16 to identify matches between the observed retention time patterns of the sample and the various compound categories. For example, Figure 21 shows a good match between sample retention times and the alcohol category, while Figure 22 shows that there is not a good match with the aldehyde category. Use of the overlay approach identified ketones, in addition to alcohols as the only good fit to the retention time data for sample mixture.

From this evaluation the four HPLC methods and the one GC method shows promise as a screening technique. The utility of the elution profile scheme is however restricted to the categories of compounds used to construct the profiles. At least for samples that are not extremely

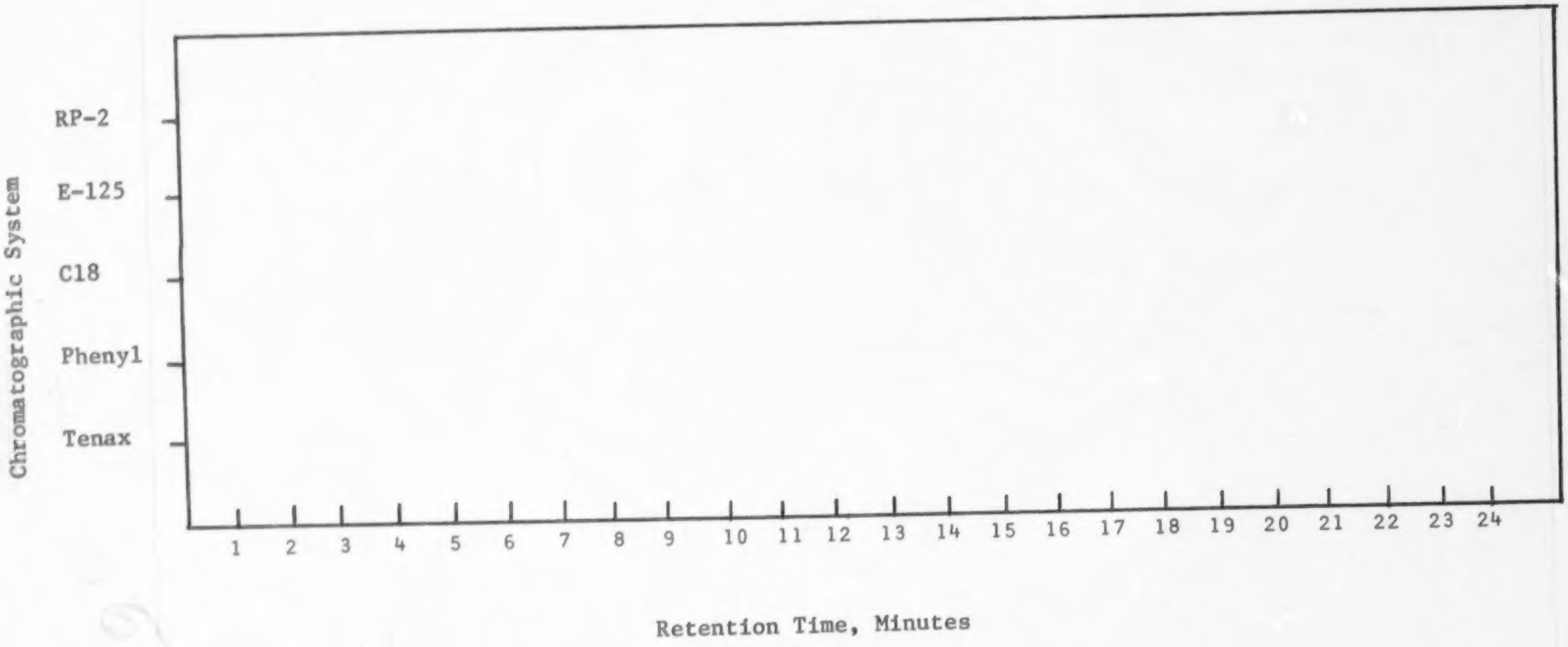

FIGURE 19: Blank Grid for Preparing Retention Time Overlay

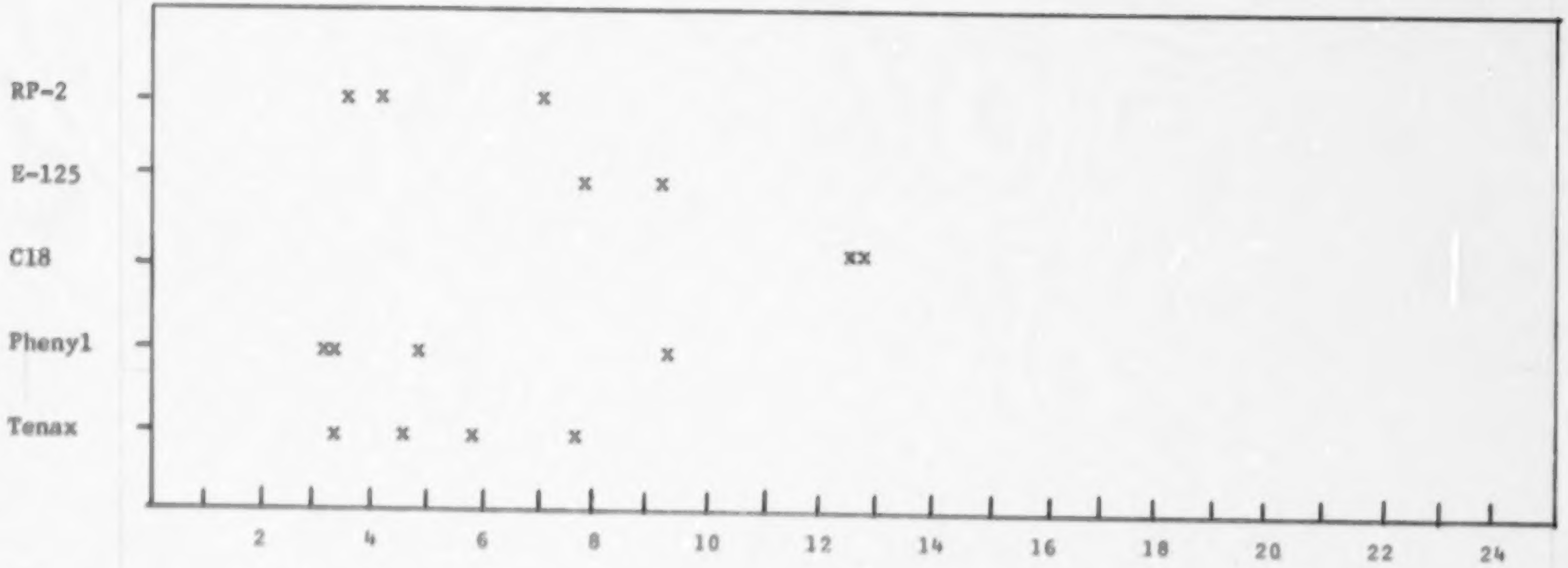

FIGURE 20: Example of Overlay Pattern for Unknown Sample Mixture

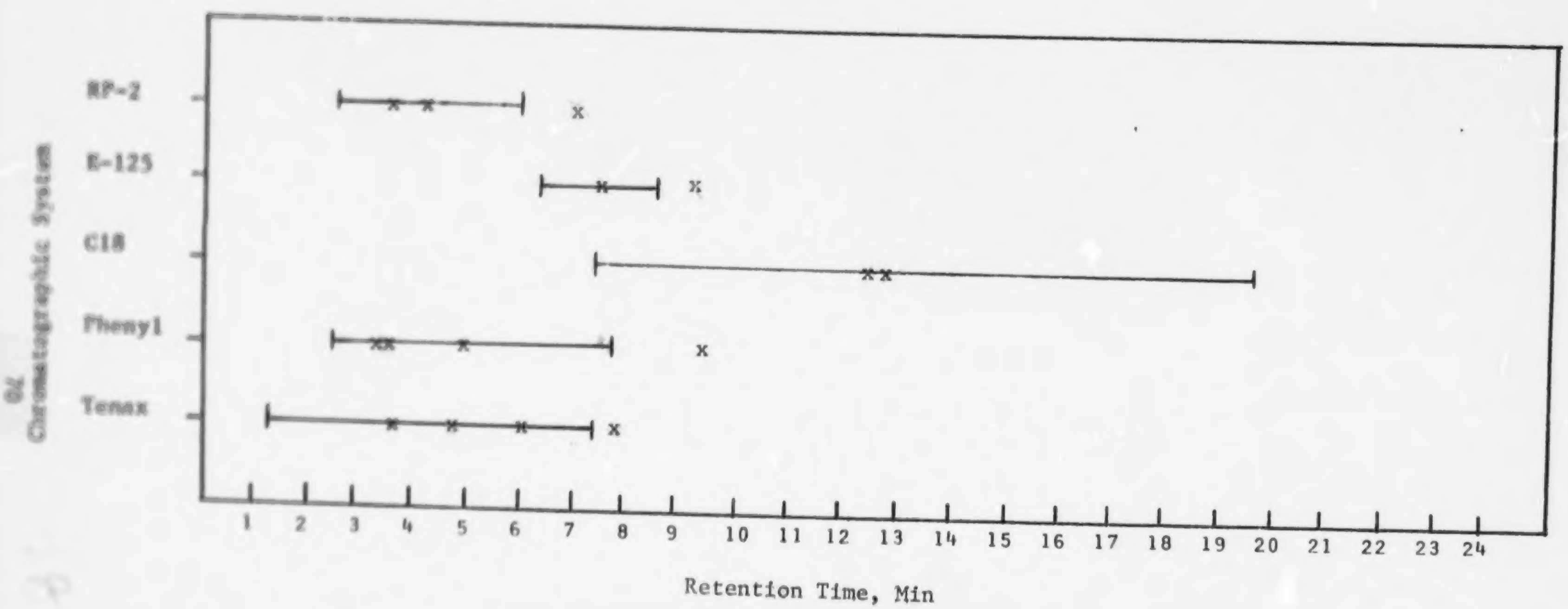

FIGURE 21: Overlay of Sample Retention Times (Figure VI-17) onto Elution Profile for Alcohols Category (Figure VI-7). (Crosses show sample peaks while lines indicate retention time windows for cateogry; note overlap in all 5 systems).

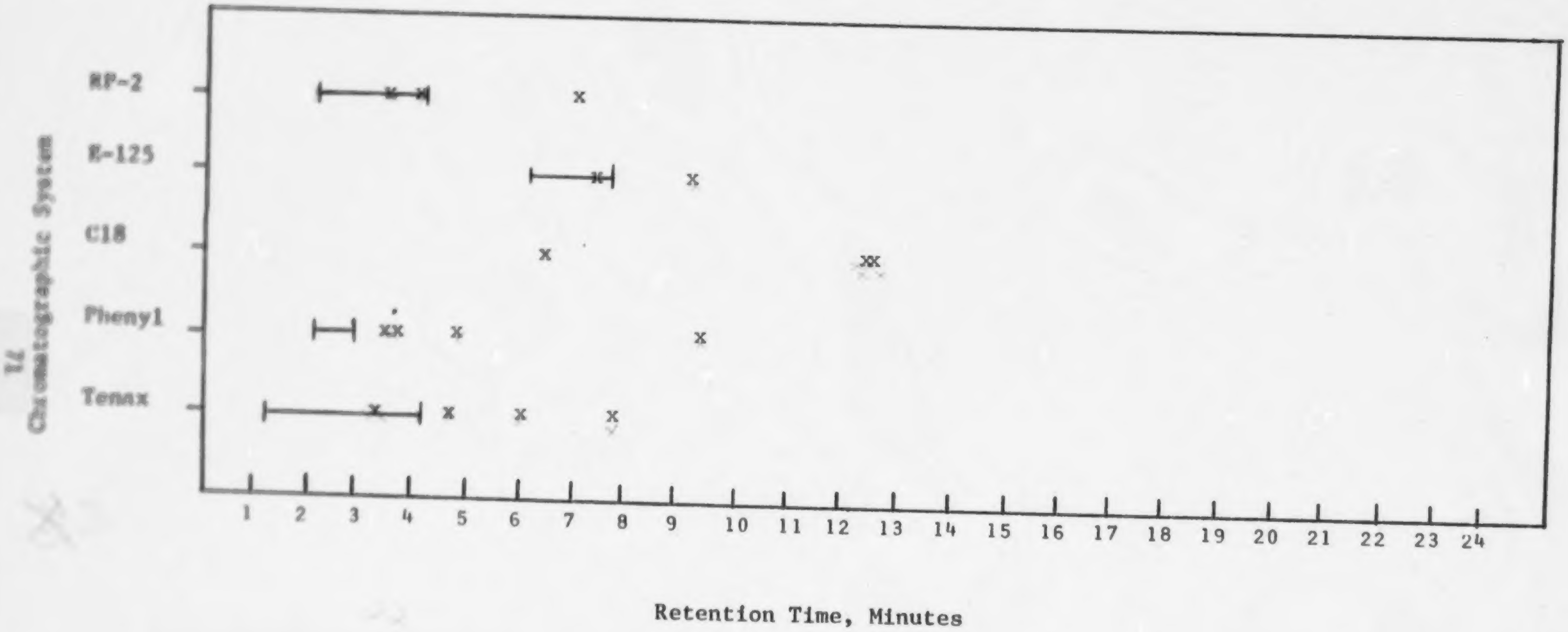

FIGURE 22: Overlay of Sample Retention Times (Figure VI-17) onto Elution Profile for Aldehydes (Figure VI-8). (Crosses show sample peaks while lines indicate retention time windows for category; note lack of overlap in C18 and Phenyl systems).

complex the set of five retention time values suffices to uniquely place the component into one of the nine compound categories. For identification based on the absence of retention time data, as in the case of the amine category, additional information is required to substantiate this selection and this approach will not work for the detection of the amine compound category.

## 3. DAI of Unknown Environmental Sample and Quality Control Data

In addition to the Test Mixture, two environmental aqueous groundwater samples and corresponding quality control samples were evaluated. The procedures for the spiking, extraction and analysis are described below.

The following list identifies the 100 mL aliquots of samples and spikes that were analyzed:

- Unknown Environmental Sample 1
- Unknown Environmental Sample 1 spike
- Unknown Environmental Sample 2
- Blank Milli-Q Water Spike
- Blank Milli-Q Water

A 500 µL aliquot of the following stock solution was added to 100 mL of sample and blank to provide the spiked QC samples.

| | | Concentration | |
|---|---|---|---|
| | | in stock solution | in spiked sample |
| Spiking Solution | Ethanol | 10 mg/mL | 50 mg/L |
| | Diethyl Glycol | 10 mg/mL | 50 mg/L |
| | Phenol | 10 mg/mL | 50 mg/L |

The samples, QC samples and blanks were extracted, purged, filtered and analyzed on each of the five systems. The sample retention time data are listed in Table 18 and the tabulated QC data presented in Table 19.

Only one peak on only one column (C-18) was identified for Environmental Sample 1. The long retention time on the C18 HPLC system suggest that this component has a relatively high affinity for organic media compared to water, which is the mobile phase in this system. This suggests the presence of a component which is not one of the model water soluble organics identifiable by the elution profile scheme. This may represent a small residue in the aqueous sample of a component that was largely extracted by the methylene chloride procedure.

Environmental sample 2 contains at least one component detectable by each one of the chromatographic systems. A comparison of the data to the elution profiles in Figures 2 to 7 or 8 to 15 strongly suggests the presence of an alcohol. At least one other component exists in sample 2 based on the detection of a peak at 14.5 minutes in the E-125 system. The lack of additional retention time data eliminates the water soluble model compounds as possible idntities.

The quality control data shows that deection and recovery for ethanol and diethylene glycol in both the spikd Milli-Q water and the environmental sample cases are quite good. Tere is a very good correlation between the data obtained for the clea water spike and the environmental spike.

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## TABLE 18

### Environmental Sample Retention Time Data

| | RP-2 (min) | E-125 (min) | C18 (min) | Phenyl (min) | Tenax (min) |
|---|---|---|---|---|---|
| Environmental Sample 1 | - | - | 27.4 | - | - |
| Environmental Sample 2 | 2.6 | 6.7/14.5 | 7.6 | 2.4 | 1.2 |

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## TABLE 19

## Quality Control Data

| | Chromatographic System | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | RP-2 | | E-125 | | C18 | | Phenyl | | Tenax | |
| | Conc mg/L | % recovery | Conc mg/L | % recovery | Conc mg/L | % recovery | Conc mg/L | % recovery | Conc mg/L | % recovery |
| **Blank Spiked (50 ppm)** | | | | | | | | | | |
| Ethanol | 53.8 | 108 | 46.6 | 93 | 58.2 | 116 | 53.0 | 106 | 44.4 | 89 |
| Diethylene glycol | 47.7 | 95 | 30.4 | 61 | 45.0 | 90 | 45.3 | 91 | ND | |
| Phenol | ND | - | 8.0 | 16 | ND | - | 6.3 | 13 | 16.9 | 34 |
| **Environmental Sample 1 Spike* (50 ppm)** | | | | | | | | | | |
| Ethanol | 50.5 | 101 | 46.6 | 93 | 53.2 | 106 | 51.1 | 102 | 52.1 | 104.2 |
| Diethylene glycol | 44.8 | 90 | 30.4 | 61 | 45.0 | 90 | 44.0 | 88 | ND | - |
| Phenol | ND | - | 8.0 | 16 | ND | - | 9.3 | 19 | 17.4 | 35 |

*Environmental Sample 1 was analyzed on each of the above systems. No peaks were detected at the retention times of ethanol, diethylene glycol or phenol.

Diethylene glycol was not detected in the Tenax system because of the lack of sensitivity at this concentration level. Phenol exhibits poor recovery due to losses from sample extraction and volatility during sample handling.

## 4. DAI Summary

Elution profiles were produced by chromatographing model compounds of water soluble organics on five chromatographic systems. Precision, accuracy, and the detection limit for these systems were determined. The profiles were exploited to identify unknown compound mixtures and environmental samples. The usefulness of this five-fold chromatographic system is restricted to those categories of compounds used to construct the elution profiles. This method of identification is applicable to actual waste samples if the number and type of "non-extractable" water soluble organics in the sample is limited. The aqueous purged portion of the organic solvent extracted sample will contain the water soluble organics of interest for further analysis with some losses of the volatile constituents.

It should be noted that the DAI-elution profile scheme is applicable primarily for the detection of moderate concentrations (10s to 100s of mg/L) of water soluble organics. This concentration range seems appropriate for application to aqueous effluent streams in light of the relatively low toxicity of most of these materials. The DMEG values for water soluble organics are sufficiently high to render the refractive index detector suitable as a detection system in this scheme, despite its relatively low sensitivity.

The same data (Table 9) generated to support the DAI-elution profile scheme also indicate which of the five chromatographic systems provide good resolution of specific compounds within the various compound categories. The system/category combinations that cover relatively large ranges of retention time would be most suitable for quantitative analysis of compounds within a category. These are listed in Table 20.

Chromatograms of each category of compounds on the system which permits the best separation of compounds within that category have been included in Appendix 2. In addition, chromatograms of the unknown environmental sample and the spiked unknown environmental sample chromatographed on each of the five systems has been included.

## TABLE 20

## Chromatographic Systems that Provide Good Separation of Compounds Within Categories

| Category[a] | Chromatographic System |
|---|---|
| Acids | RP-2 |
| Alcohols | Phenyl |
| Aldehydes | Tenax |
| Amino Acids | C18 |
| Carbohydrate | C18 |
| Glycols | C18 |
| Ketones | Tenax |
| Phenols | Phenyl |

---

[a] The amine category has not been included in view of the lack of applicability the elution profile scheme has to this category of compound.

## 5. DA1 CONCLUSIONS

The objective of this task was to develop an analytical method for the separation and detection of "non-extractable" water soluble organics. The elution profile approach utilizing the five-fold retention time data from the direct aqueous injection on several chromatographic systems was investigated as a means to identify water soluble organics. Evidence for a positive identification is supported when the five-fold retention time data for one compound category match in each of the five chromatographic systems. For at least 8 of the 9 categories investigated the method shows promise as a screening technique. The current documented proof, however, is restricted to the categories of compounds used to construct the profiles. Because of the difficulty encountered in detecting the compounds in the amine category, the elution profile scheme presently has little utility in positively identifying this group of compounds. The method is applicable to actual environmental waste samples if the number and type of "non-extractable" water soluble organics is limited. Its application lies primarily in the detection of moderate concentrations of water soluble organics. In light of the relatively low toxicity of most of these materials, this concentration range seems appropriate for application to aqueous effluent streams. The data generated to support the DAI-elution profile scheme also indicate which of the chromatographic systems provide good resolution of specific compounds within the various compound categories.

## PART II: ADDITIONAL AREAS OF INVESTIGATION

### 1. Summary

The additional areas that were investigated during this program included: TOC/HPLC measurements to monitor the organic content of the aqueous sample during sample handling. The two methods correlate well in the determination of percent losses during extensive sample manipulation, however, total organic carbon was inadequate in estimating the magnitude of the concentration of water soluble organic material present in an aqueous matrix.

Freeze drying was investigated as a method to concentrate water soluble organic alcohols of various volatilities and molecular weights. The experiment demonstrated that this technique should be limited in application and used only to concentrate organic compounds which have very low vapor pressures and/or are solids.

To determine whether water soluble organics would be amenable to Level 1 analysis procedures of isolation fromthe aqueous media, water soluble organic compounds were subsequently analyzed by Level 1 LC-IR-LRMS and by GC/FTIR. Although the model compounds were insoluble in the initial LC solvent, they eluted as expected in LC 5, 6 and 7 and were detectable by Infrared and Low Resolution Mass Spectrometry procedures as discussed in the experimental portion of the report.

Colorimetric detection system using Molish, Anthrone and Ninhydrin tests were evaluated for their sensitivity and selectivity for detecting carbohydrate and amino acid compound categories. The Molish test exhibited selectivity for detecting carbohydrates in mixtures containing other categories of compounds. The detection limit of the Molish test is lower than 30 mg/L. Both the Anthrone and Ninhydrin tests lacked selectivity when evaluated with mixtures containing additional categories of compounds.

## 2. INTRODUCTION

The second part of this report describes the additional areas investigated during the program. The various topics represented potential methods which would provide additional information in assessing the water soluble organic content of an aqueous sample. These preliminary investigations included Total Organic Carbon (TOC) measurements and High Performance Liquid Chromatography (HPLC) to trace the concentration sample handling procedures. Freeze drying was evaluated as a viable method to concentrate water soluble alcohols from an aqueous matrix and colorimetric procedures which detect classes of organic compounds in aqueous matrices were examined for their sensitivity and selectivity. The categories of compounds for which these tests were investigated include carbohydrates and amino acids.

Additionally, Level 1 procedures were investigated to determine how well Level 1 analysis methods would work if the water soluble organics could be recovered from the aqueous solution. Several water soluble model compounds were "forced" through the Level 1 procedures. One of the objectives of this portion of the study was to determine what types of additional information would be obtained to assist in characterizing a sample for these compounds if they could be recovered from the aqueous solution.

Lastly, a method is reported for the detection and quantification of linear alkylbenzene sulfonates in a complex aqueous matrix. Table 21 summarizes the areas of investigation reported in Part 2 of this report.

## TABLE 21

## Additional Areas of Investigation

Part 2

- TOC/HPLC Measurements, Sample Handling
- Concentration of Water Soluble Organic Alcohols by Freeze Drying
- Colorimetric Detection Systems
- Level 1 Application/GC/FTIR
- Specific Analytical Method for LAS in Complex Aqueous Matrix

Alternatives for the concentration and separation of water soluble organics from an aqueous matrix which were not explored in this work include resins, ion-exchange and "other" organic extracting solvents. Resins and extracting solvents were not considered by reason of the poor extraction recoveries for the water soluble organics predicted by the partition coefficients for these systems. Ion-exchange had been evaluated in the Master Analytical Scheme and has shown limited usefulness due to the high conductivity of environmental water samples. In addition, ion-exchange requires extensive sample manipulation and exhaustive recovery studies to ensure sample integrity.

## 3. EXPERIMENTAL

### A. EXPERIMENTAL DETAILS

This section describes materials and instrumentation used and presents experimental details for each of the areas outlined in Table 21.

#### 1. Materials

- Solvents: Methanol, Methylene Chloride, Pentane, HPLC grade
- Colorimetric Reagents and Indicators: Anthrone, α-Napthol, Ninhydrin, Methyl orange, reagent grade.
- Nitrogen, 99% purity, Air Products Corp.
- Filters, Millipore type HA, 0.45 µm mixed cellulose acetate/nitrate
- Acid 6N $H_2SO_4$ (Fisher)
- Base 6N NaOH (Fisher)
- pH paper
- Silica Gel, Davison, 60-200 mesh, grade 950, Fisher Scientific Company
- Linear alkylbenzene sulfonates
- Sephadex G 10 Resin, Pharmacia
- Tetramethylammonium chloride 97%, Aldrich, used without further purification.
- Water, distilled, deionized water obtained from systems such as Millipore Milli-Q® System
- Glassware:

  Syringes, 250 µL, 100 µL, 10 µL

  Volumetric flasks, sufficient to prepare calibration standards

Volumetric pipettes
Separatory funnels, 250 mLs, 1L
Glass sparging device
Chromatographic column, open glass with teflon stopcock.

- Hot Plate
- High Performance Liquid Chromatographic Columns: HC-ODS SIL-X, 5 μm Perkin Elmer
- Gas Chromatographic column
  10% OV 101 on 100/120 Supelcoport, 6' x 4 mm id glass, Supelco
  or
  10% SP 2100 on 80/100 Supelcoport, 6' x 4 mm id glass, Supelco

## 2. Instruments

- TOC Analyzer, Dohrmann, Model DC-50/52, Environtech Corp.
- Freeze Drier
- Infrared Analyzer, Perkin Elmer Model 621 dispersive instrument
- GC/FTIR, Digilab Mode FTS-15C Fourier Transformer Infrared Spectrometer, Varian Model 3700 Gas Chromatograph
- Mass Spectrometer: DuPont CEC-110B with batch inlet and direct insertion probe interfaced to DC Eclipse 200 data system.

## 3. Analytical Methods

Analytical Methods - Total Organic Carbon HPLC Measurements, Sample Handling.

The aqueous mixtures were prepared and stored in amber bottles and refrigerated for one week. Initial 2 mL portions were withdrawn from the samples for analysis prior to storage. The samples were then extracted as prescribed in the Level 1[17] manual. The aqueous samples were then purged to remove residual methylene chloride, and analyzed according to the modified Level 1 procedures for TOC analysis[18] on this contract. The Dohrmann analyzer was used for TOC measurements; the chromatographic system RP-2 described in Table 7 was used for confirmation.

## Analytical Methods - Concentration of Water Soluble Organic Alcohols by Freeze Drying.

Two hundred milliliter aliquots of each solution containing selected alcohols at 3 concentration levels were concentrated to < 10 mL by freeze drying. In addition, a Milli-Q water blank was concentrated to < 10 mL. The concentrated solutions were brought to volume in 10 mL volumetric blanks with Milli-Q water and analyzed by the RP-2 HPLC procedure in Table 7 injection 100 µL volumes.

## Analytical Methods - Level 1 Application, GC/FTIR

A test mixture containing the model compounds listed below was placed directly onto the top of an LC column prepared according to Level 1 applications.

| Compound | Weight (mg) |
|---|---|
| Glucose | 5.9 |
| Sorbitol | 4.7 |
| Malonic Acid | 3.7 |
| Triethanolamine | 23.8 |
| Glycerol | 34.0 |

(cont)

| Compound | Weight (mg) |
|---|---|
| Ethylene glycol | 20.4 |
| Formaldehyde | 4.1 |
| Methyl Ethyl Ketone | 4.0 |
| Isopropanol | 3.9 |
| Ethanol | 3.9 |
| Cyclohexanone | 4.7 |
| Phenol | 3.7 |
| Sucrose | 6.3 |
| Citric Acid | 5.2 |
| Total | 128.3 mg |

The elution sequence, TCO, IR and LRMS procedures of the Level 1 manual were followed.

The compounds were placed directly onto a bed of 6 grams of silica gel in a glass column. The compounds were placed directly on the column due to their insolubility in the recommended solvent, cyclopentane. The seven Level 1 fractions were collected and injected on a gas chromatograph for TCO determination. Three hydrocarbon standards, $C_9$, $C_{12}$ and $C_{16}$ at three concentration levels 15 $mg/ml^{-1}$, 1.5 $mg/ml^{-1}$ and 0.15 $mg/ml^{-1}$ were used to standardize the system. The chromatographic conditions used for analysis are listed below.

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Total Chromatographable Organic (TOC) Analysis

Hewlett Packard GC/FID
10% OV-101, 6' x 4 mmid glass column
30°C isothermal 6 minutes
20°C/minute→250°C; 20 minutes
2 µL injection volume

In addition, GC/FTIR analyses using the following conditions were performed on fractions 5, 6 and 7.

Digilab FTS-15C Fourier Transform Infrared Spectrometer
Column: 10% SP 2100 on 80/100 Supelcoport
Temperature Program: 30° for 5 minutes
5°/min → 275°C for 20 minutes
Injector Temperature: 250°C
Transfer Lines: 300°C
Light Pipe: 300°C
Infrared Detector: Wide band mercury cadmium telluride (MCT)

Infrared data was collected using a spectral resolution of 8 $cm^{-1}$. Computer software was used which automatically picked GC peaks from the infrared reconstruction.

## Analytical Methods - Colorimetric Detection Systems, Specific

### Analytical Methods

Aqueous solutions containing the individual carbohydrates and amino acids listed below were exposed to three specific colorimetric detection tests at the specified concentration levels.

| | H-1 (ppm) | H-2 (ppm) | H-3 (ppm) | H-4 (ppm) | H-5 (ppm) |
|---|---|---|---|---|---|
| Sucrose | 0 | 92.2 | 1073 | 18.4 | 9.2 |
| Fructose | 992 | 107.3 | 0 | 21.5 | 10.8 |
| Mannose | 0 | 102.7 | 0 | 20.5 | 10.2 |
| Glucose | 0 | 102.5 | 0 | 20.5 | 10.2 |

| | G-1 (ppm) | G-2 (ppm) | G-3 (ppm) | G-4 (ppm) |
|---|---|---|---|---|
| L-Proline | 214 | 64.2 | 21.4 | 10.7 |
| β-Alanine | 251 | 75.4 | 25.1 | 12.6 |
| DL-Methionine | 205 | 61.5 | 20.5 | 10.2 |

In addition, the following mixtures were prepared and exposed to the same colorimetric tests.

Mix 1

50 ppm each compound in the following compound categories from Table 5: Acid, Alcohol, Aldehyde, Amino Acid, Carbohydrate, Ketone, Phenol, and Amine.

Mix 2

Same as Mix 1 excluding the Carbohydrate category.

Mix 3

Same as Mix 1 excluding the Amino Acid category.

The test solutions were then exposed to the appropriate reagents for the compound category of interest using the following procedures.

Carbohydrates

Molish Reagent: 10% α Naphthol in Methanol

Procedure: Place 1 drop of reagent solution with one drop of aqueous sample solution. Allow the above mixture to run down the side of a test tube containing 0.3

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mL of concentrated $H_2SO_4$ to form an interfacial layer. A positive test gives a violet-purple color at interface.

Anthrone Reagent: 0.1% Anthrone in conc. $H_2SO_4$

Procedure: Add 0.5 mL of aqueous solution to 0.5 mL reagent solution. A positive test gives a blue ring.

Amino Acids

Ninhydrin Reagent: 0.2% Ninhydrin in 90% Ethanol in water

Procedure: Place 1 mL of aqueous sample and 1 mL of reagent in a test tube. Insert test tube in a beaker of boiling water and bring mixture to boil. A positive test gives blue-purple reaction.

# 4. RESULTS AND DISCUSSION

## 4.A TOC, HPLC MCEASUREMENTS SAMPLE HANDLING

Solutions of model alcohol compounds in water were used to determine the magnitude of losses introduced during handling of the sample and the usefulness of Total Organic Carbon (TOC) measurements as a means of monitoring the organic content of the aqueous sample. Two aqueous mixtures containing model compounds were used for this evaluation, the compounds used and their concentration levels are listed in Table 21. The samples were initially measured for Total Organic Carbon and analyzed by High Performance Liquid Chromatography. Figures 23 and 24 show the HPLC separation of these two sample mixtures. The samples were then stored in amber bottles refrigerated for 1 week and extracted as prescribed in the Level 1 manual. The aqueous sample was then purged to remove residual methylene chloride.

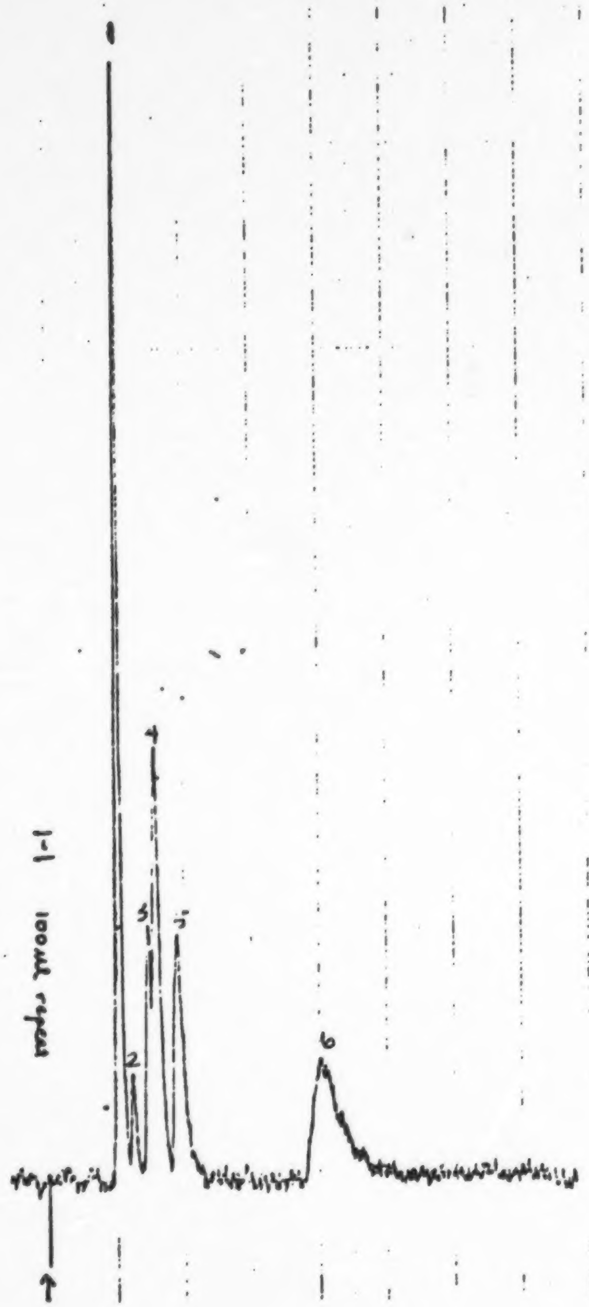
Table 22 summarizes the percent losses calculated for each individual component as quantified by the HPLC procedure. Table 23 summarizes the percent losses calculated from the TOC data including a comparison to the cumulative losses calculated in Table 22. Overall the percent losses calculated by the two independent methods correlate well, indicating that TOC measurements can be used to monitor the organic carbon content of aqueous samples for losses of material. The losses that are observed were all less than 30% and can be attributable to a combination of extraction and extensive handling of the sampling. The TOC measurements of the initial solutions and concentration data for the

## TABLE 22

## Concentration Data for Sample Solutions

| | Solution 1 | Solution 2 | Solution 3 | Solution 4 |
|---|---|---|---|---|
| Methanol | 554 | 118.7 | | |
| Ethanol | 552.5 | 118.4 | | |
| Isopropanol | 549.8 | 117.0 | | |
| 1-Butanol | 566.9 | 121.5 | | |
| Sorbitol | 500 | 125.0 | | |
| Ethylene glycol | | | 554.4 | 138.6 |
| Diethylene glycol | | | 559.8 | 140.0 |

* Concentration in mg/L mg/L

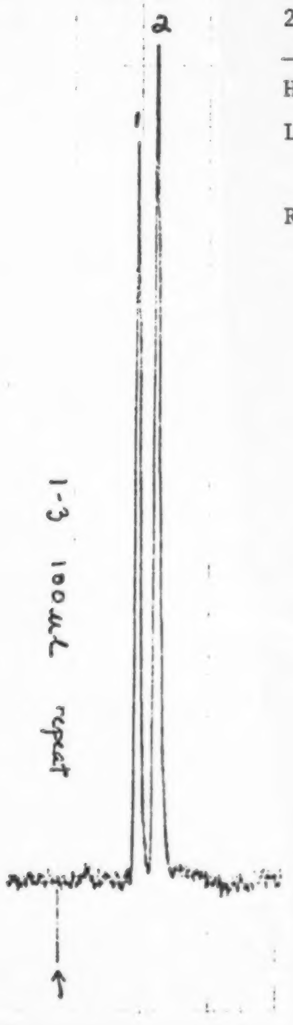


HPLC ALCOHOL MIX

1 Sorbitol
2 Methanol
3 Ethanol
4 2-Methoxyethanol
5 Isopropanol
6 1-Butanol

HPLC/RI
LiChrosorb RP-2
1.5 mL min $^{-1}$ $H_2O$
RI 4 X
Injection volume 100 µL

FIGURE 23:



HPLC Glycol Mix

1. Ethylene glycol
2. Diethylene glycol

HPLC/R1

LiChrosorb RP-2

1.5 ml min$^{-1}$ $H_2O$

RI 4 x

injection volume 100µl

FIGURE 24:

24

## TABLE 23

### Percent Loss on Extraction Calculated from HPLC Data

| Compound | Molecular Weight | Boiling Point | Percent Loss Calculated by HPLC | | | |
|---|---|---|---|---|---|---|
| | | | Soln (1) | Soln (2) | Soln (3) | Soln (4) |
| Methanol | 32.04 | 64.96 | 0 | 17 | | |
| ETOH | 46.07 | 78.5 | 10 | 3 | | |
| Isopropanol | 60.11 | 82.4 | 20 | 25 | | |
| 1-Butanol | 74.12 | 117.25 | 53 | -[a] | | |
| Sorbitol | 182.18 | 295 | -[b] | -[b] | | |
| 2-Methoxyethanol | 76.11 | 125 | 4 | 27 | | |
| Ethylene glycol | 62.07 | 198 | | | 0 | 0 |
| Diethylene glycol | 106.1 | 245 | | | 2.4 | 0 |

a - not able to quantify, broad peak

b - peak from HCl used to adjust pH interferes with the Sorbitol peak. However, since Sorbitol is insoluble in $CH_2Cl_2$ it is unlikely that any removal from the water phase occurred.

## TABLE 24

## Per Percent Loss Detected by TOC Compared to HPLC

| | Detected | Percent Loss | Percent Loss by HPLC |
|---|---|---|---|
| Initial TOC of soln 1 | 180.76[a] | 20.0 | 14.5 |
| Final TOC of aqueous extract of soln 1 | 143.26[b] | | |
| Initial TOC of soln 2 | 368.33 | 19.0 | 12.0 |
| Final TOC of aqueous extract of soln 2 | 298.53 | | |
| Initial TOC of soln 3 | 459.31 | 0.9 | 2.4 |
| Final TOC of aqueous extract of soln 3 | 455.03 | | |
| Initial TOC of soln 4 | 108.56 | 0 | 0 |
| Final TOC of aqueous extract of soln 4 | 111.96 | | |

[a] diluted 1:10; TOC reading of undilted sample 1807.6

[b] diluted 1:10; TOC reading of undilted sample 1432.6

individual components in the solution are listed in Table 25. The comparison shows that the TOC measurements made of the mixtures do not indicate the magnitude of the alcohol concentration, since alcohols have a low carbon content compared to hydrocarbons of comparable carbon number or molecular weight.

If the concentrations listed in Table 25 are corrected based on the actual percent carbon available, the values obtained for TOC do agree well with the corrected carbon based concentrations. Total organic carbon is an adequate measure for monitoring the organic carbon content of an aqueous sample. It suffers in its application to water soluble organics since the TOC measurements do not indicate the magnitude of the concentration present. For at least the alcohol category, an additional measure of concentration is necessary.

## TABLE 25

### Comparison of TOC Data to the Concentration of the Samples Prepared*

| | Weight % Carbon | Solution 1 | Solution 2 | Solution 3 | Solution 4 |
|---|---|---|---|---|---|
| MeOH | 37.4 | 554 | 118.7 | | |
| ETOH | 52.2 | 552.5 | 118.4 | | |
| Isopropanol | 60.0 | 549.8 | 117.0 | | |
| 1-Butanol | 64.9 | 566.9 | 121.5 | | |
| Sorbitol | 37.7 | 500 | 125.0 | | |
| 2-Methoxyethanol | 47.4 | 625.3 | 144.7 | | |
| Ethylene glycol | 38.7 | | | 554.5 | 138.6 |
| Diethylene glycol | 45.3 | | | 559.8 | 140.0 |
| Sum of Organic Component Concentrations | | 3350 | 745 | 1110 | 279 |
| Sum of Carbon Content for Components: | | 1680 | 375 | 468 | 117 |
| TOC Measurement | | 1810 | 368 | 459 | 109 |

---

* Concentration in mg/L

## 4.B CONCENTRATION OF WATER SOLUBLE ORGANIC ALCOHOLS BY FREEZE-DRYING

Freeze-drying was evaluated as a means of concentrating several model water soluble alcohols in water. The following solutions were prepared:

| | A (mg/L) | B (mg/L) | C (mg/L) |
|---|---|---|---|
| Methanol | 11.1 | 158.3 | 554.0 |
| Ethanol | 11.0 | 157.9 | 552.5 |
| Isopropanol | 11.0 | 157.1 | 549.8 |
| 2-Methoxyethanol | 13.5 | 192.9 | 625.3 |
| Sorbitol | 10.0 | 125.0 | 500.0 |

The HPLC analysis of the concentrated solutions revealed that only the sorbitol remained in mixes B and C after the freeze-drying process. The sorbitol in the concentrates was determined and compared to the initial concentration to calculate the percent losses attributable to the process.

| | Initial Concentration (mg/L) | Final Equivalent Concentration (mg/L) | % Loss after Freeze-Drying |
|---|---|---|---|
| Sorbitol | 500 | 470 | 6 |
| Sorbitol | 125 | 120 | 4 |

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The loss of all compounds except sorbitol exemplified the limitations of freeze-drying for the range of compounds of interest in the elution profile scheme. Freeze-drying is applicable for the concentration of those components from water which have very low vapor pressures and/or are solids.

## 4.C. LEVEL 1 APPLICATION, GC/FTIR

Several water soluble organic compounds were "forced" through the Level 1 procedure to determine if additional information is obtained which would assist in characterizing a sample for these compounds. The compounds in Table 26 were eluted from a Level 1 silica gel column. Total chromatographable organic determination, Infrared Analysis, LRMS and GC/FTIR were performed on each fraction. Since all model compounds used were TCO range materials, no GRAV analyses were performed.

Table 26 lists the compounds and their initial weights used for the Level 1 and GC/FTIR application. The compounds were placed directly on a bed of 6 grams of silica gel in a glass column. The compounds were placed directly on the column because of their insolubility in the usual Level 1 solvent (cyclopentane). The seven fractions were collected using the Level 1 LC elution scheme and subsequently analyzed by Gas Chromatography for total chromatographable organics. The concentrations observed for each of the fractions are tabulated in Table 27.

This Level 1 approach indicates the area of concentration was located in fractions 5, 6 and 7 for the water soluble organics, as would be expected.

Infrared spectra of the seven fractions were obtained. The interpretations are detailed in the following IR reports in Appendix 3. Fraction seven seemed to contain the most material. All the spectra showed evidence of alphatic C-H and C-O of alcohols. Some fractions showed weak carbonyl bands.

95

## TABLE 26

## Compounds Used for Level 1 and GC/FTIR Application

| Compound | Initial Weight (mg) |
|---|---|
| Glucose | 5.9 |
| Sorbitol | 4.7 |
| Malonic Acid | 3.7 |
| Triethanol Amine | 23.8 |
| Glycerol | 34.0 |
| Ethylene glycol | 20.4 |
| Formaldehyde | 4.1 |
| Methyl Ethyl Ketone | 4.0 |
| Isopropanol | 3.9 |
| Ethanol | 3.9 |
| Cyclohexanone | 4.7 |
| Phenol | 3.7 |
| Sucrose | 6.3 |
| Citric Acid | 5.2 |
| TOTAL | 128.3 |

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97

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21

## TABLE 27

### TCO Values Observed in Level 1
### LC Separation of Synthetic Mixture

| LC Fraction | TCO Found in Fractions (mg) |
|---|---|
| 1 | 0.54 |
| 2 | 3.29 |
| 3 | 2.60 |
| 4 | 4.22 |
| 5 | 15.2 |
| 6 | 38.96 |
| 7 | 42.7 |
| Total | 107.51 |

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98

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The seven LC fractions were also subjected to GC/FTIR. The compounds identified in each fraction were:

| LC Fraction | Compound Identification |
|---|---|
| 1 | substituted butanes |
| 2 | substituted butanes |
| 3 | substituted butanes |
| 4 | an amine |
| 5 | |
| 6 | cyclohexanone, phenol |
| 7 | ethylene glycol, glycerin |

Absence of the other compounds may be attributable to their low concentration and/or their lack of volatility.

Low Resolution Mass Spectral data was obtained for the LC fractions which contained detectable material. The LRMS reports follow in Appendix 4.

The water soluble organic compounds were forced through the Level 1 procedure to determine if the information obtained would allow for the characterization of a fraction containing water soluble organic material. Table 28 summarizes the results. From the analyses, the methanolic fractions contain the highest concentration of material and exhibit the most activity in the infrared. The assignments of the wave numbers for the early eluting fractions identify primary and secondary alcohols with some carbonyl overtones of ketones. The later eluting fractions, 5, 6 and 7 reflect the character of the polar fractions containing polyhydric alcohols, overtones from glucose

30

## TABLE 28

## Comparison of Water Soluble Compounds/Categories Present in Mixture with Results of Level 1 Analysis

| Compounds Present | Detected by Level 1 |  | Detected by |
|---|---|---|---|
|  | IR | LRMS | FT/IR |
| **Alcohols, Glycols** | ✓ | ✓ |  |
| Ethanol |  |  |  |
| Isopropanol |  |  |  |
| Glycerol | ✓ |  | ✓ |
| Ethylene glycol |  |  | ✓ |
| **Carbohydrates** |  |  |  |
| Glucose |  | ✓ |  |
| Sucrose |  |  |  |
| Sorbitol |  |  |  |
| **Aldehydes, Ketones** | ✓ |  |  |
| Formaldehyde |  |  |  |
| Methyle ethyl ketone |  |  |  |
| Cyclohexanone |  |  | ✓ |
| **Phenols** |  |  |  |
| Phenol | ✓ | ✓ | ✓ |
| **Acids** |  |  |  |
| Citric Acid |  |  |  |
| Malonic Acid |  |  |  |
| **Amines** |  | ✓ | ✓ |
| Triethanolamine |  |  |  |

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and the tentative identification of glycerol in fraction 7. No inference is made to the range of components that were spiked onto the silica gel column. Several components could have been lost during the sample preparation for IR analysis. The higher molecular weight and non-volatile species are characterized by the application of Level 1, but the carboxylic acids, ketones, and simple aliphatic alcohols were not specifically identified as categories present by either IR or LRMS techniques. This result is at least a preliminary indication that the usual Level 1 procedures are not especially well suited to analysis of low molecular weight polar species that constitute the majority of water soluble organics even if those species are isolated from the aqueous matrix.

GC/FTIR was also used to evaluate the fractions collected from the Level 1 silica gel column. Direct injection of the fractions provided identification of a substantial amount of material that had been spiked on to the LC column. This method of analysis has great utility in providing additional information for the water solubles scheme. The drawbacks are analogous to the restrictions of Chromatographic System Tenax and limited to the sample spectra contained in the library.

## 4.D COLORIMETRIC DETECTION SYSTEMS, SPECIFIC ANALYTICAL METHODS

There exist several colorimetric procedures which identify classes of organic compounds. Most of the methods are not applicable to the direct analysis of water. However, three tests without this restriction were evaluated for their utility in identifying the presence of carbohydrate and amino acids compounds. The sensitivity of these methods were investigated in addition to the limits of their usefulness when a mixture containing other categories of compounds are present.

The three tests investigated were:

Molisch test - carbohydrates

Anthrone test - carbohydrates

Ninhydrin test - amino acids

The procedures used for the tests and preparation of reagents are outlined in the experimental Details V.B.

The following designations symbolize the solutions prepared for the colorimetric tests as outlined in section V.B. 7, the results of which are reported in Table 29.

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| | H-1 (ppm) | H-2 (ppm) | H-3 (ppm) | H-4 (ppm) | H-5 (ppm) |
|---|---|---|---|---|---|
| Sucrose | 0 | 92.2 | 1073 | 18.4 | 9.2 |
| Fructose | 992 | 107.3 | 0 | 21.5 | 10.8 |
| Manose | 0 | 102.7 | 0 | 20.5 | 10.2 |
| Glucose | 0 | 102.5 | 0 | 20.5 | 10.2 |

| | G-1 (ppm) | G-2 (ppm) | G-3 (ppm) | G-4 (ppm) |
|---|---|---|---|---|
| L-Proline | 214 | 64.2 | 21.4 | 10.7 |
| β-Alanine | 251 | 75.4 | 25.1 | 12.6 |
| DL-Methionine | 205 | 61.5 | 20.5 | 10.2 |

Mix 1

50 ppm each compound in the following compound categories from Table 10 22: Acid, Alcohol, Aldehyde, Amino Acid, Carbohydrate, Ketone, Phenol, and Amine.

Mix 2

Same as Mix 1 excluding the carbohydrate category.

Mix 3

Same as Mix 1 excluding the Amino Acid category.

The usefulness of any analytical detection system is dependent on the specificity of the method. Mixtures which contain compounds from different categories of compounds may interfere with the mechanism to yield false/negative results. This is the case with the majority of existing colorimetric methods. The Molish test is a sensitive and specific procedure for the detection of carbohydrates in mixtures and environmental samples. The Anthrone and Ninhydrin tests which were evaluated are severely limited in specificity. The Anthrone test was not sensitive to total carbohydrate levels of 400 ppm or lower. The Ninhydrin test is sensitive for the detection of amino acids above about 30 ppm but looses its usefulness in the presence of other categories of compounds. If additional data supports the presence of amino acids, the Ninhydrin test may confirm its presence.

## TABLE 29

### Results of Colorimetric Tests

| Test: | Molish | | Anthrone | | Ninhydrin | |
|---|---|---|---|---|---|---|
| Result: | Expected | Obs'd | Expected | Obs'd | Expected | Obs'd |
| **Test Mixture** | | | | | | |
| H-1 (1000 ppm total)[a] | + | + | + | + | | |
| H-2 (400 ppm total)[a] | + | + | + | - | | |
| H-3 (1000 ppm total)[a] | + | + | + | + | | |
| H-4 (80 ppm total)[a] | + | + | + | - | | |
| H-5 (40 ppm total)[a] | + | + | + | | | |
| G-1 (800 ppm total)[b] | | | | | + | + |
| G-2 (200 ppm total)[b] | | | | | + | + |
| G-3 (65 ppm total)[b] | | | | | + | + |
| G-4 (33 ppm total)[b] | | | | | + | - |
| Mix 1 (50 ppm)[c] | + | + | + | - | + | - |
| Mix 2 (50 ppm)[d] | - | - | - | - | + | - |
| Mix 3 (50 ppm)[e] | + | + | + | - | - | - |

[a] Total Carbohydrates

[b] Total Amino Acid

[c] 50 ppm each compound in Table 10 from the following categories: Acid, Alcohol, Aldehyde, Amino Acid, Carbohydrate, Ketone, Phenol, and Amine

[d] 50 ppm each compound as in c. except the carbohydrate category

[e] 50 ppm each compound as in c. except the amino acid category

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The Molish and Ninhydrin colorimetric procedures could be usefully applied to some aqueous samples to obtain additional information which will assist in characterizing a sample.

## 4.E Specific Analytical Method for Linear Alkybenzene Sulfonates (LAS)

To supplement the elution profile and colorimetric detection systems, a review of a method for the separation and detection of linear alkylbenzene sulfonates, which are expected to be relatively commonly encountered in effluents because of their use as surfactants, has been included.

Linear alkylbenzene sulfonates (LAS) are part of the sulfonic acid group. A method[19] previously developed to analyze for LAS in complex aqueous matrices was reviewed for its application for its analyses in other aqueous media. For some samples a less rigorous sample clean-up procedure would suffice. The aqueous matrix used in this study contained water, fats, proteins and carbohydrates. Six aqueous mixtures were spiked with linear alkylbenzene sulfonates. The samples were subjected to a set of extraction and clean-up procedures delineated below. The average recoveries for the six samples were 77% with a CV of 0.079. Figure 25 is an outline of the initial procedure to which the sample is subjected. This procedure removes most of the high molecular weight fats and proteins present and concentrates the LAS in a smaller volume.

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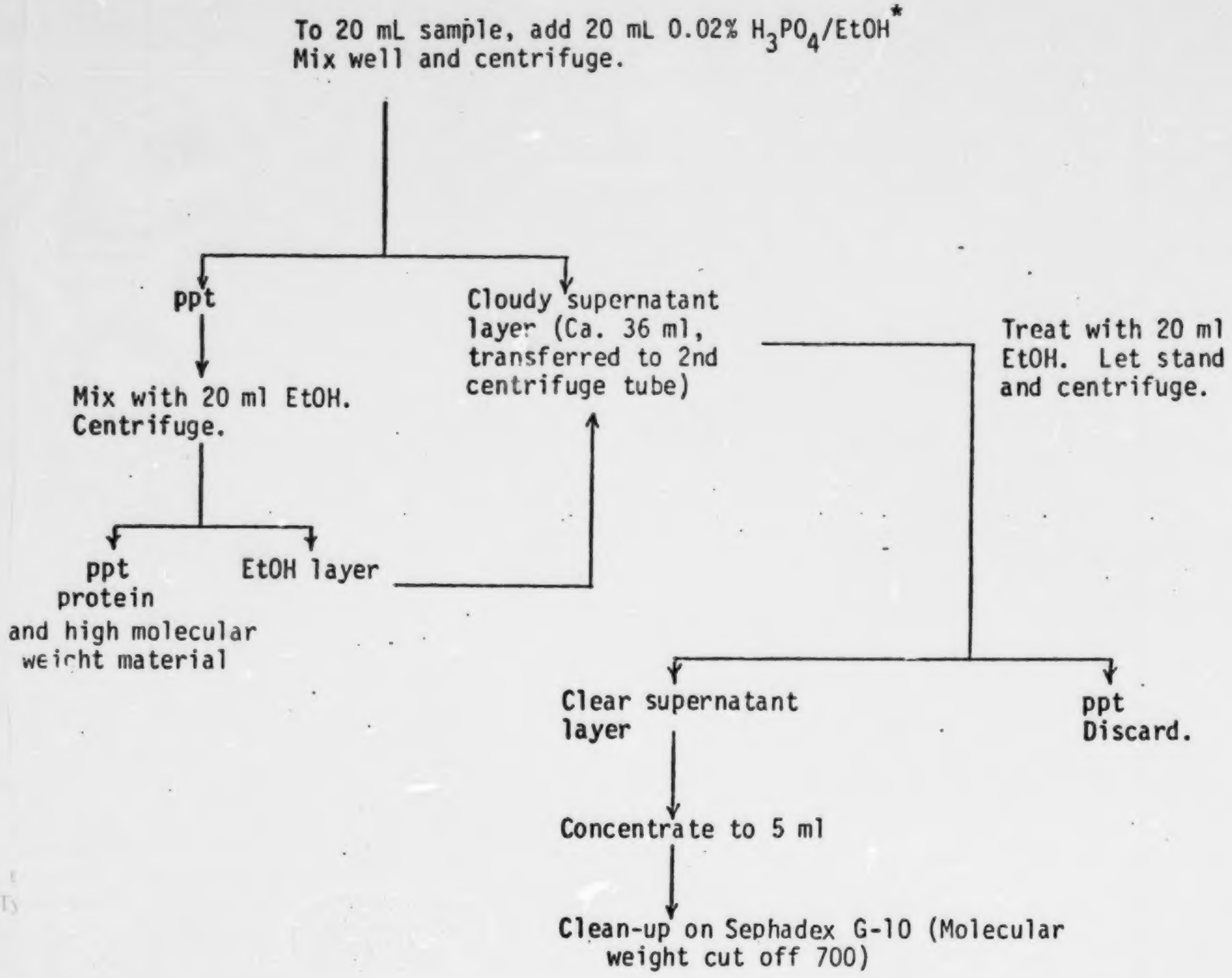
Methyl orange was used as a visual aid to monitor the extraction and separation procedure in the hopes that the LAS would behave in a similar manner since they are both from the sulfonic acid category. The concentrated sample was then separated using a Sephadex G-10 column. The


To 20 mL sample, add 20 mL 0.02% $H_3PO_4$/EtOH*
Mix well and centrifuge.
ppt
Cloudy supernatant layer (Ca. 36 ml, transferred to 2nd centrifuge tube)
Treat with 20 ml EtOH. Let stand and centrifuge.
Mix with 20 ml EtOH. Centrifuge.
ppt protein and high molecular weight material
EtOH layer
Clear supernatant layer
ppt Discard.
Concentrate to 5 ml
Clean-up on Sephadex G-10 (Molecular weight cut off 700)

*EtOH is USP 190° Proof.

25

FIGURE 25: Extraction/Isolation of LAS from a Complex Aqueous Matrix

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Sephadex G-10 resin was allowed to swell in distilled deionized water and then slurry-packed into an open glass column. The packing material was then washed with several column volumes of 70/30 methanol/$H_2O$. Table 30 outlines the elution pattern of LAS and methyl orange from a sample concentrate. Fractions 4, 5, and 6 were analyzed using a high performance liquid chromatographic system developed for the analysis of LAS and were found to contain the species of interest. These fractions were then combined and concentrated by gentle heat and nitrogen flow.

The HPLC conditons for LAS were:

| | |
|---|---|
| Column: | Perkin Elmer HC-ODS Sil-X 5 micron |
| Mobile Phase: | 0.015M tetramethylammonium chloride in 80/20 MeOH-$H_2O$, pH 2.8 (adjusted with $H_2SO_4$) |
| Flow Rate: | 1.0 mL $min^{-1}$. |
| Injection Volume: | 30 μL |
| Detector: | UV λ222 nm, x 0.02 Absorbence Units Full Scale(AUFS) |
| Chart Speed: | 0.2 in. $min^{-1}$ |

The chromatographic conditions can be altered to give maximum resolution between the individual LAS. Figure 26 shows two chromatograms of LAS standards. It was found that the complexity of the matrix can sometimes introduce (or induce) extra column effects on the chromatography of the sample. Far better resolution was obtained when a standard was prepared in a sample blank. A sample blank consists of the aqueous matrix (sample blank) that was not spiked with either methyl orange or LAS and put through the entire scheme to be used as a blank for the system. When this "sample

32

## TABLE 30

## Elution Patterns on Sephadex G-10

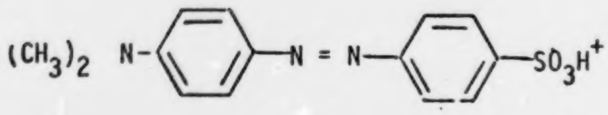
Column Dimension: 10 cm x 22 mm I.D.

Solvent: MeOH/$H_2O$ (70:30)

Sample Size: 2.5 mL of sample concentrate containing 100 μg methyl orange (Visual Aid) and 200 μg LAS.

| Fraction No. | Sequential Effluent Volume | Description of Fraction | Observations |
|---|---|---|---|
| 1 | 1-10 ml | clear | MO band moves slowly as a narrow band. At 10th ml, $R_f$= 0.28 and band width is 0.5 cm. |
| 2 | 10-20 ml | cloudy | At 18th ml, methyl orange $R_f$=0.58; band width is 1 cm. |
| 3 | 20-25 ml | clear | At 22nd ml, methyl orange $R_f$=0.83; band width = 1.3 cm. |
| 4 | 25-30 ml | yellow-orange | At 26th ml, methyl orange band begins to elute. |
| 5 | 30-35 ml | yellow-orange | Rest of methyl orange band elutes. |
| 6 | 35-40 ml | v.light yellow | |

Methyl orange



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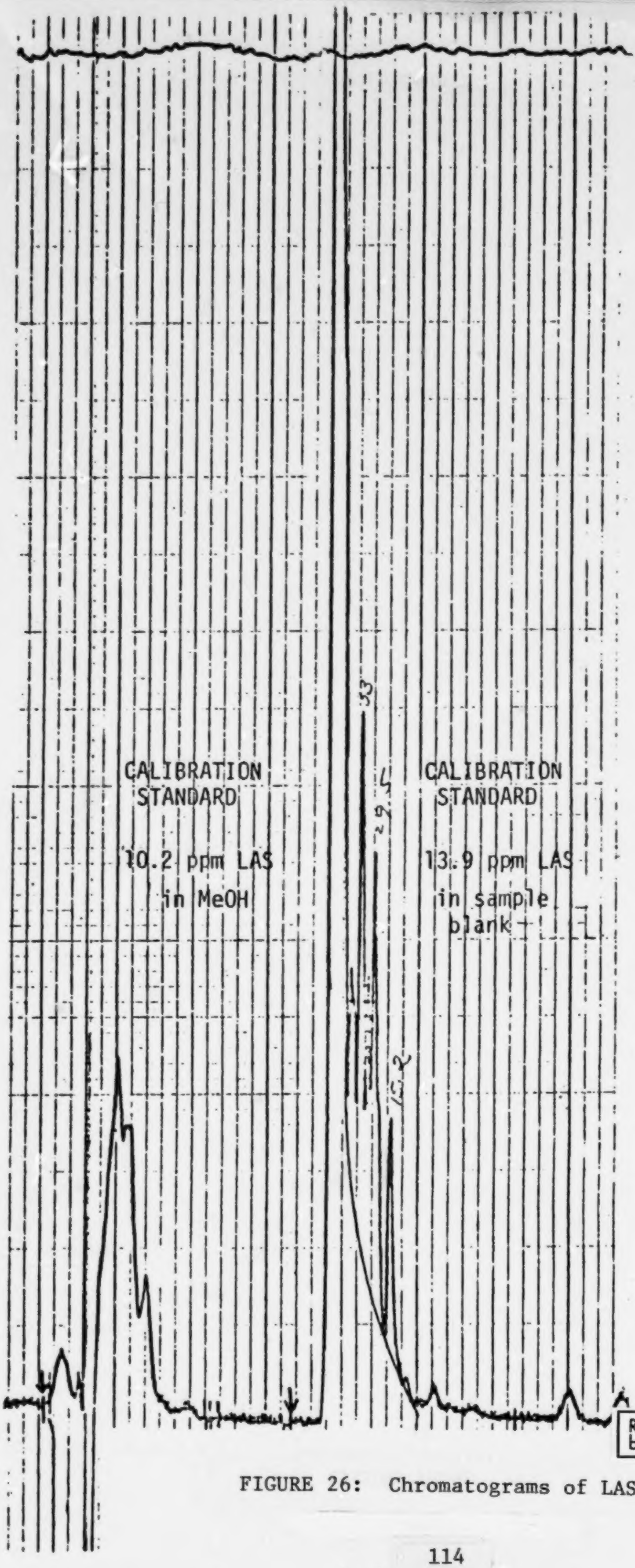

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FIGURE 26: Chromatograms of LAS

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blank" was chromatographed alone, no peaks were observed where the LAS would elute. Figure 27 shows the chromatograms obtained for a sample blank and two spiked samples. Calibration curves can be prepared from any one or a combination of the LAS peaks. The calibration curve used to obtain the analytical data for a series of spiked samples is presented in Figure 28 and the results can be found in Table 31. These results show that the method can be used to analyze for linear alkylbenzene sulfonates at low ppm levels in aqueous matrices.

The specific chromatographic methods for the analysis of linear alkylbenzene sulfonates has been extensively applied to environmental samples. The method is sensitive and directly applicable to complex aqueous matrices; it is recommended for application when the specific detection of the LAS category is required.

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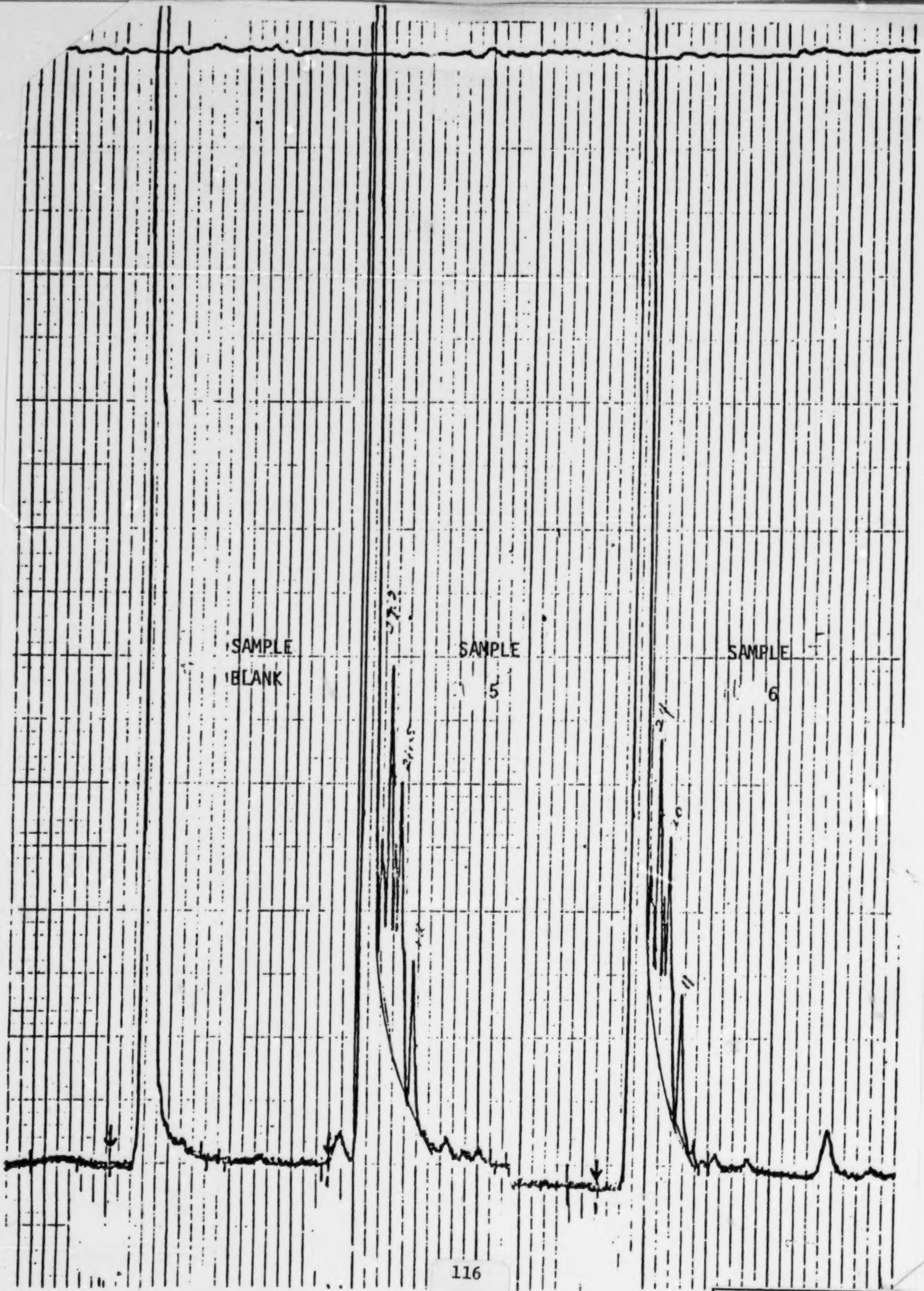

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FIGURE 27: Sample Chromatograms

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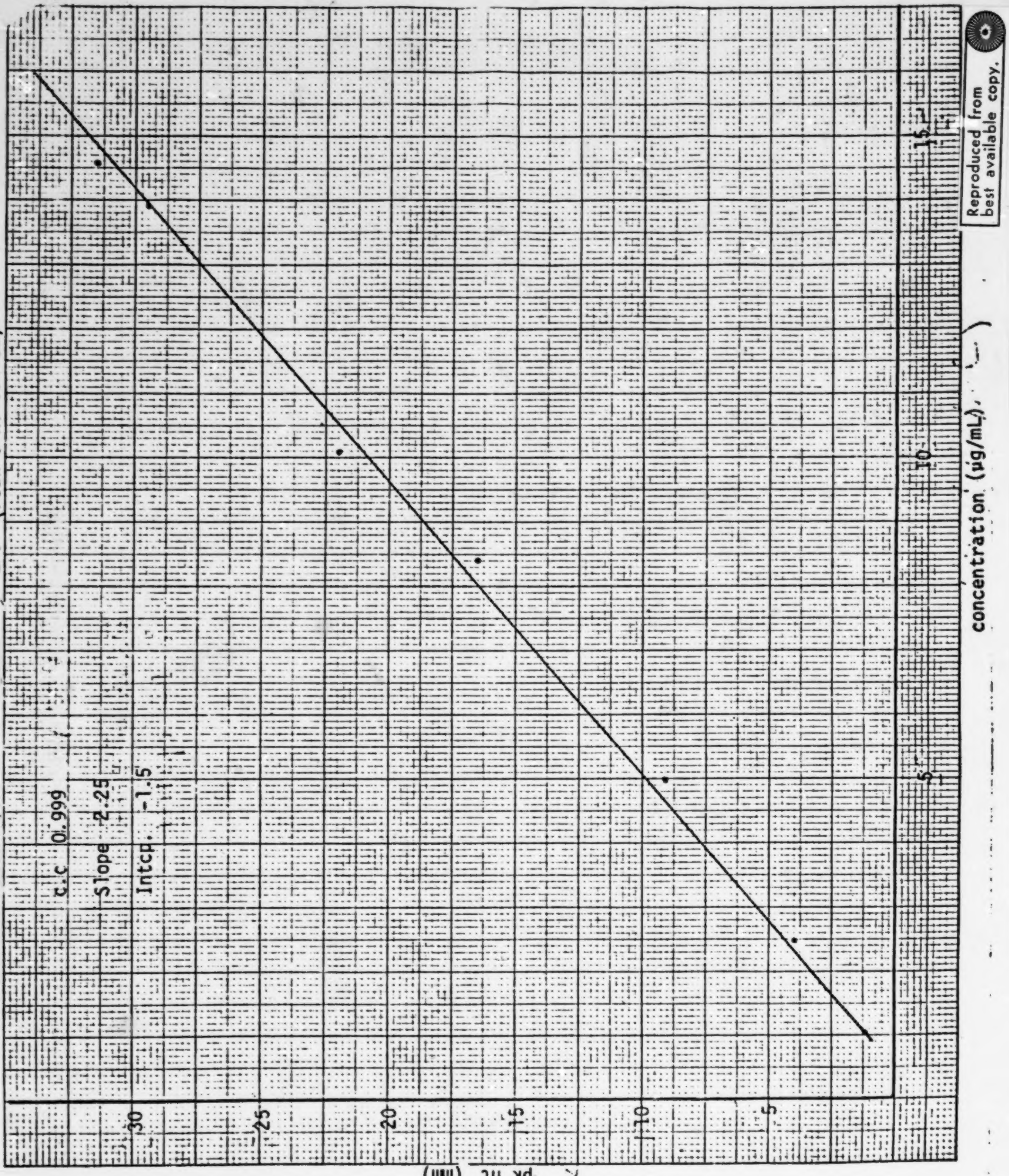

FIGURE 28: Calibration Curve for LAS

33

## TABLE 31

### Analysis of LAS in a Complex Aqueous Matrix

Sample: 25 mL Sample "spiked" with the LAS at 10.3 ppm

| SAMPLE CODE | μg ADDED | μg FOUND | % RECOVERY |
|---|---|---|---|
| 1 | 257 | 189 | 73.5 |
| 2 | 257 | 189 | 73.5 |
| 3 | 257 | 179 | 69.6 |
| 4 | 257 | 212 | 82.5 |
| 5 | 257 | 220 | 85.6 |
| 6 | 257 | 200 | 77.8 |
| | | AVERAGE | 77.1 |
| | | STD. DEV. | 6.07 |
| | | CV | 0.079 |

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## 5. Conclusions for Part II Investigations

Total organic carbon was investigated to determine its utility in providing the TOC content of aqueous solutions containing water soluble organic compounds. The TOC measurement can be used for monitoring the organic carbon content of an aqueous sample, however, its application suffers since the measurement does not represent the actual value of the concentration of water soluble organic material present.

Freeze drying was investigated as a method to concentrate water soluble organic alcohols from water. Final measurements show that only compounds with high vapor pressures or compounds which exist as solids are applicable to this method of concentration.

Water soluble organics were forced through the Level 1 procedure and GC/FTIR to determine if information obtained would allow for the characterization of a fraction containing water soluble organic material even if the species are isolated from the aqueous matrix. From this investigation no inference was made from the results as to the range of components that were spiked onto the silica gel column. Only the higher molecular weight and non-volatile species were characterized by the application of Level 1. The low molecular weight polar species were not specifically identified as categories present by either IR or LRMS. GC/FTIR did provide identification of a substantial amount of the material spiked onto the LC column and has utility in providing additional information for the water soluble scheme. The drawbacks here are analogous to the GC chromatographic system Tenax used in the elution profile scheme.

The colorometric procedures available can, in some instances, provide identification of compound categories with sensitivity and specificity. Three of these tests; Molish, Ninhydrin and Anthrone were examined for their utility to the model compounds used in the program. The results indicate that the Molish test for carbohydrates is both sensitive and specific for the detection of this category of compounds in mixtures and environmental samples.

A method to quantify the presence of LAS in complex aqueous matrices is provided. The method was validated and has shown average recoveries of 77% with a CV of 0.079 for six samples. The extraction and clean up procedures are detailed in the experimental section for this method.

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# APPENDIX 1[11]

The necessary partition coefficient to achieve 50 or 75% recovery can be calculated by the following equation:

$$X_n = X_o \left(\frac{W}{W+PL}\right)^n \; n$$

where

P = Partition Coefficient, $\frac{X_{org}}{X_{aq}}$

$X_n$ = final amount in aqueous solution

$X_o$ = original amount in aqueous solution

W = solution volume

L = extractant volume at each stage

n = number of stages of extraction

Solving for P in terms of $\frac{X_n}{X_o}$ (% not recovered) given in the Level 1 procedure 1 in which n=3 and L=0.05W yields:

$$P = \frac{\left(X_o/X_n\right)^{1/3} - 1}{0.05}$$

for the partition coefficient necessary to produce $\left(1-\frac{X_n}{X_o}\right)$ X 100% recovery. Solving for $\frac{X_n}{X_o}$ = 0.25 (75% recovery), we have P = 11.7. Solving for $\frac{X_n}{X_o}$ = 0.50 (50% recovery), we have P = 5.2. Thus, any compound to be extracted will require, under ideal conditions, a partition coefficient of 12 for 75% recovery, or 5 for 50% recovery.

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# APPENDIX 2

# CHROMATOGRAMS

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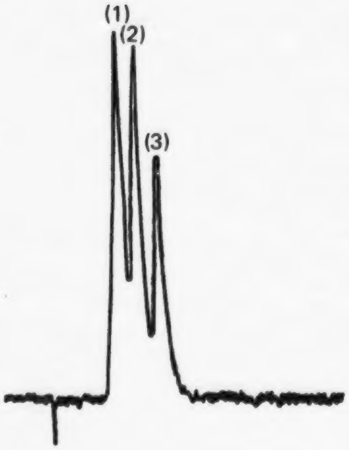
Acid Mix Cal 2
Chromatographic System RP-2
250 μL injection volume
RI 4X
Chart speed 0.2 in/min

Peaks Detected
1. Citric Acid
Malonic Acid
2. Acetic Acid
3. Propionic Acid

Peaks Detected
1 Citric Acid
Malonic Acid
2 Acetic Acid
3 Propionic Acid



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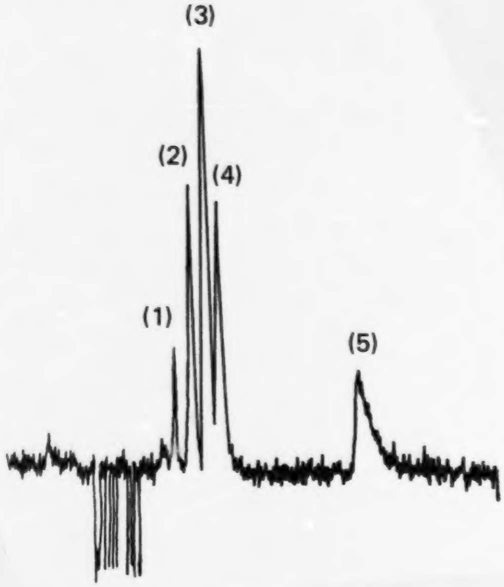
Alcohol Mix Cal 1
Chromatographic System Phenyl
100 μL injection volume
RI 2X
Chart Speed 0.5 cm/min

Peaks Detected
1. Methanol
2. Ethanol
3. Methanolethanol
4. Isopropanol
5. Butanol

Peaks Detected
1 Methanol
2 Ethanol
3 Methanolethanol
4 Isopropanol
5 Butanol



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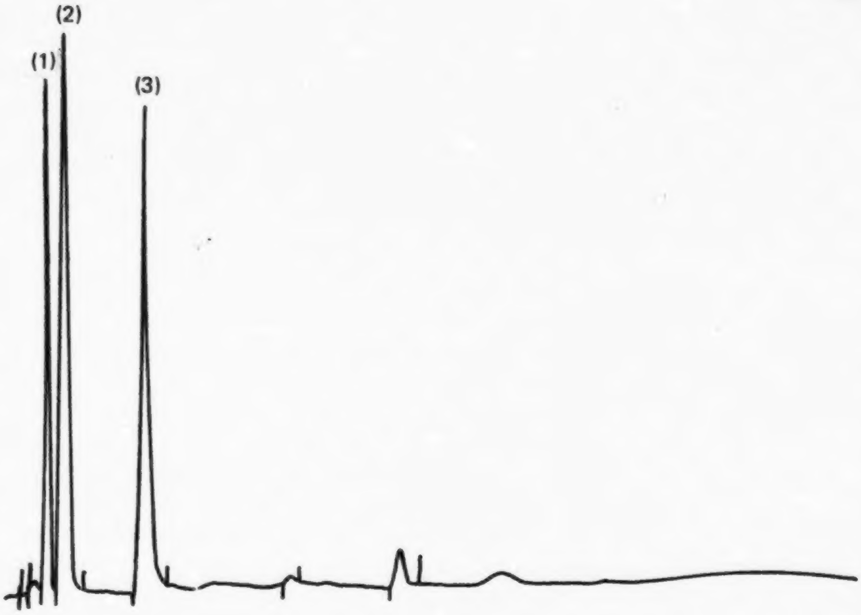
Aldehyde Calibration Mix Cal 1
Chromatographic System Tenax
2 μL injection volume
FID
Chart Speed 0.5 cm/min

Peaks Detected
1. Formaldehyde
2. Acetaldehyde
3. Propionaldehyde

Peaks Detected
1 Formaldehyde
2 Acetaldehyde
3 Propionaldehyde



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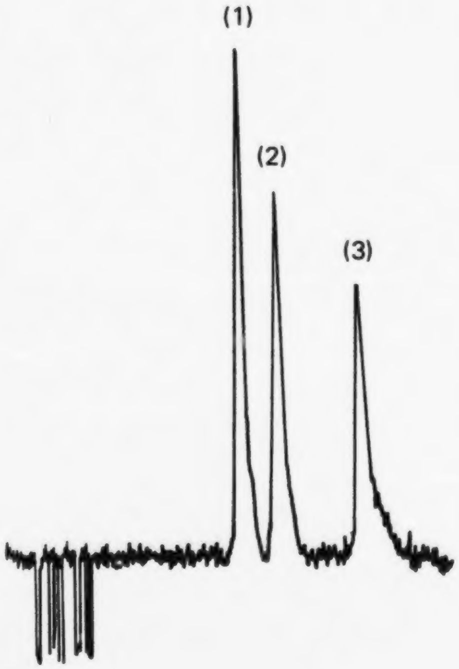
Amino Acid Mix Cal 2
Chromatographic System C18
50 µL injection volume
RI 2X
Chart speed 0.5 cm/min

Peak Detected
1. β-Alanine
2. L-Proline
3. DL-Methionine

Peaks Detected
β-Alanine
2 L-Proline
3 DL-Methionine



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132
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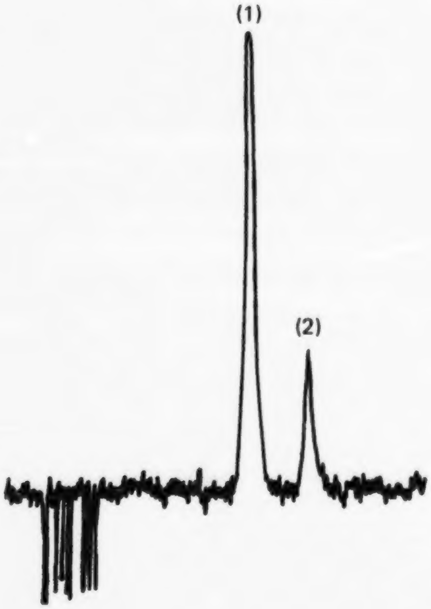
Carbohydrate Mix CAL-2
Chromatographic System C18
25 µL injection volume
RI 2 X
Chart Speed 0.5 cm/min

Peaks Detected
1. {Glucose, Fructose, Mannose}
2. Sucrose

Peaks Detected
Glucose
Fructose
Mannose

2. Sucrose



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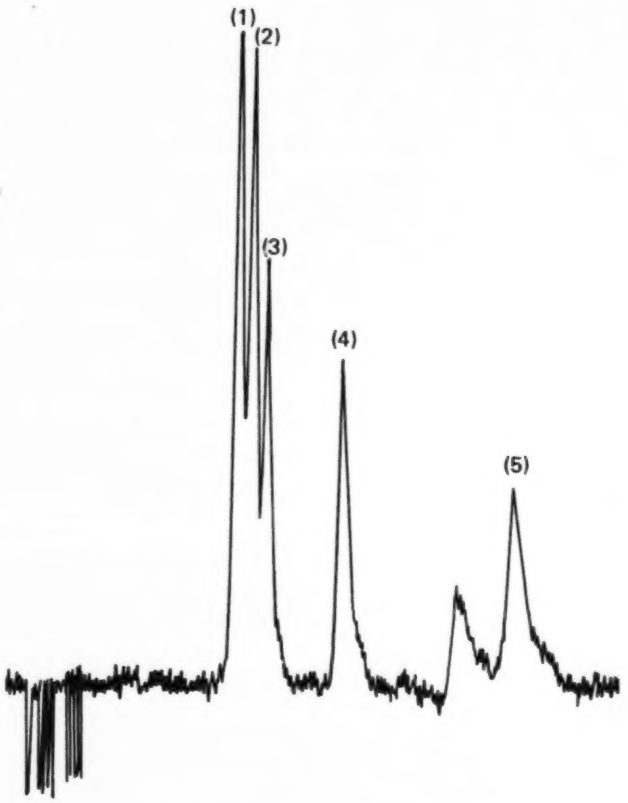
Glycol Mix CA1 5
Chromatographic System C18
50 µL injection volume
RI 2X
Chart Speed 0.5 cm/min

Peaks Detected
1. Sorbitol
2. Glycerol
3. Ethylene glycol
4. Propylene glycol
5. Diethylene glycol



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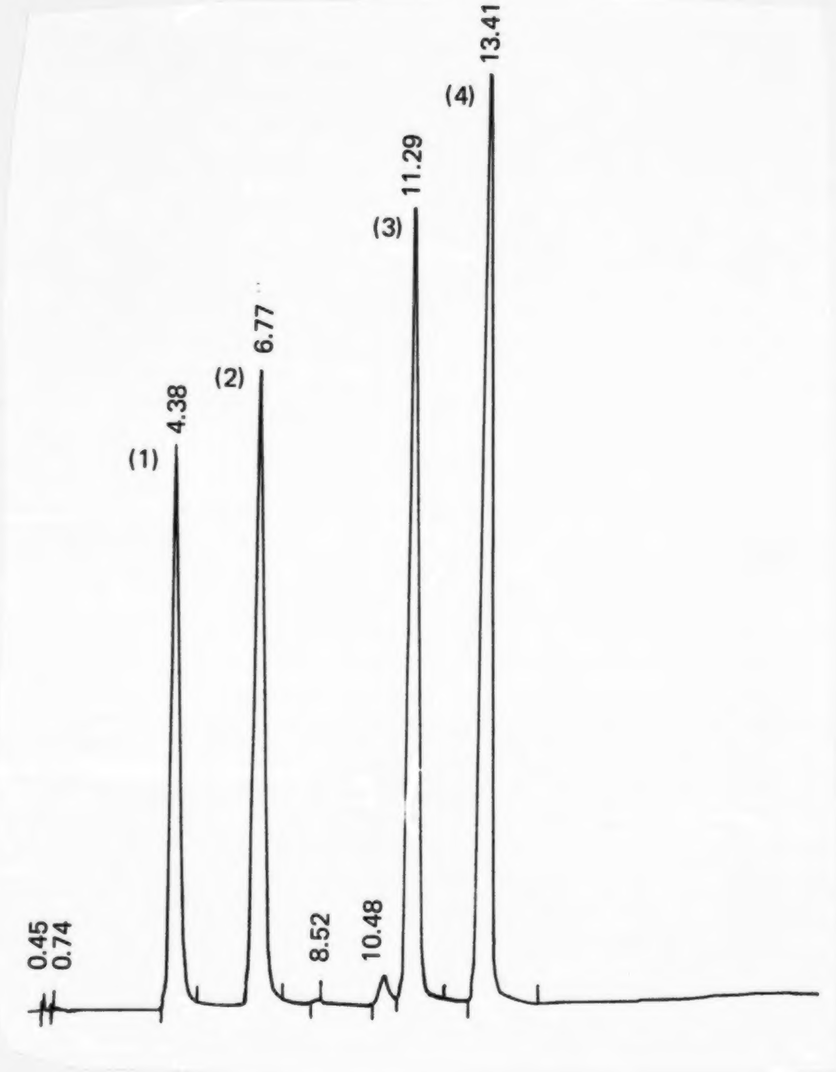
Ketone Mix Cal 1
Chromatographic System Tenax
2 μL injection volume
FID
Chart Speed 0.5 cm/min

Peaks Detected
1.Acetone
2.Methyl ethyl ketone
3.Mesityl oxide
4.Cyclohexanone

Peaks Detected
1 Acetone
2 Methyl ethyl ketone
3 Mesityl oxide
4 Cyclohexanone



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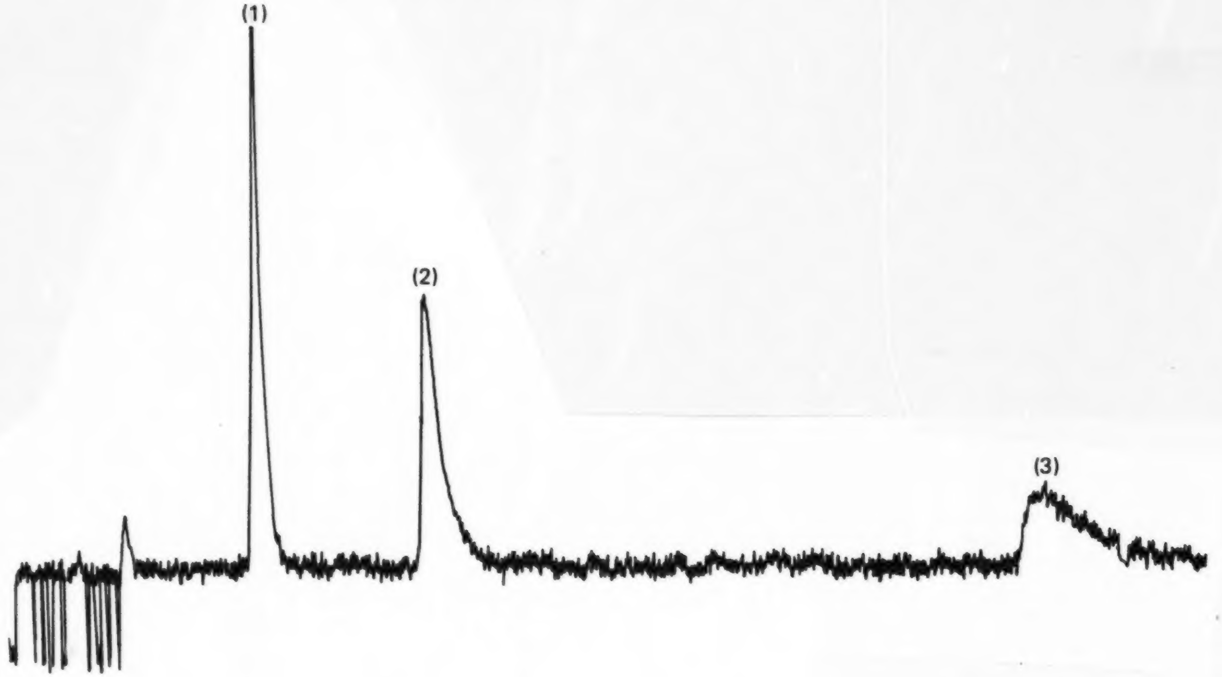
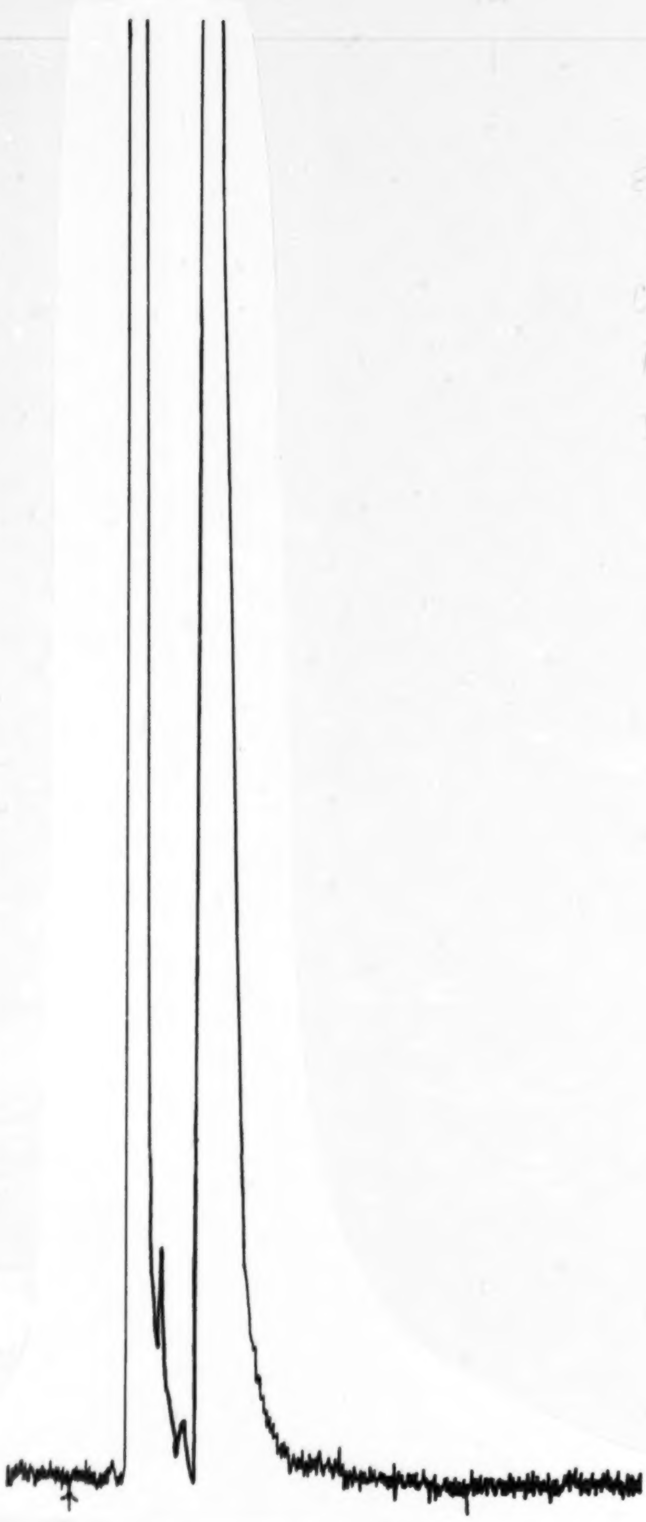
Phenol Mix Cal 1
Chromatographic System Phenyl
100 µL injection volume
RI 2X
Chart 0.5 cm/min

Peaks Detected
1. Resorcinol
2. Phenol
3. 0-Cresol



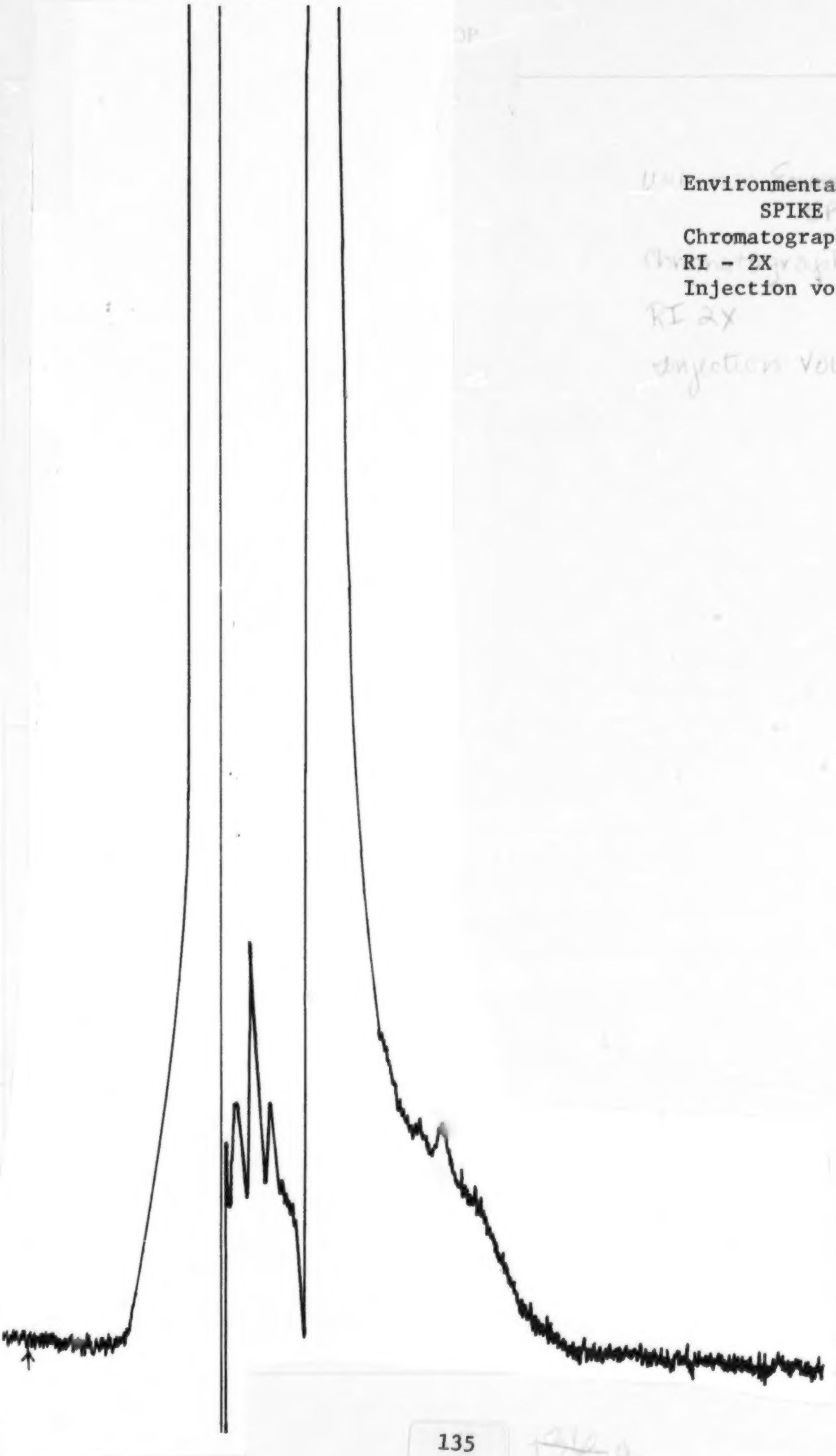


Environmental Sample 1
SPIKE
Chromatographic System RP-2
RI-2X
Injection volume 100 µL

Environmental Sample 1
Spike
Chromatographic System RP2
RI 2X
Injection volume 100µL

10 Lines
to End of
Typing Area

~~135~~ 134

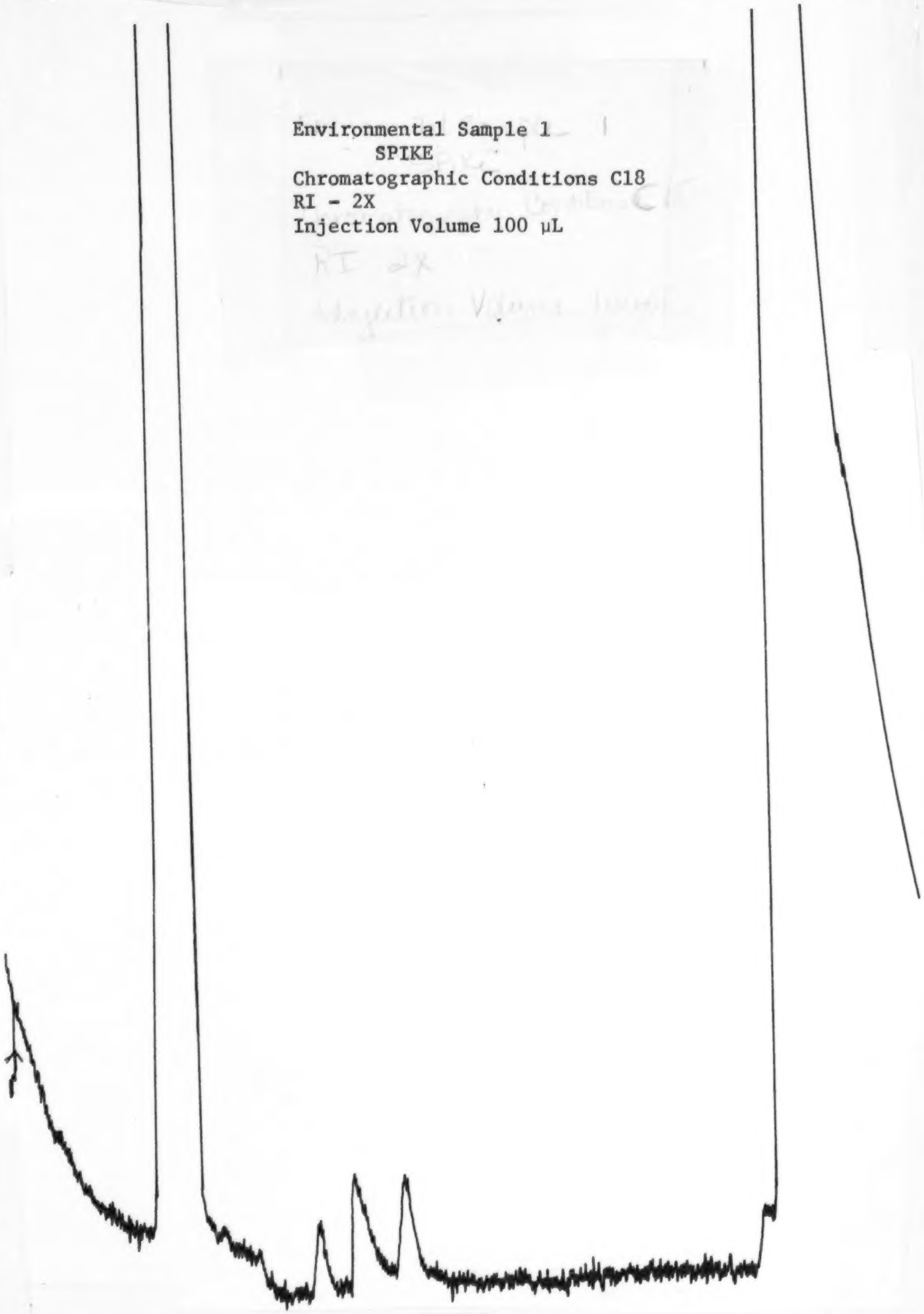


Environmental Sample 1
SPIKE
Chromatographic System E-125
RI - 2X
Injection volume 100 µL

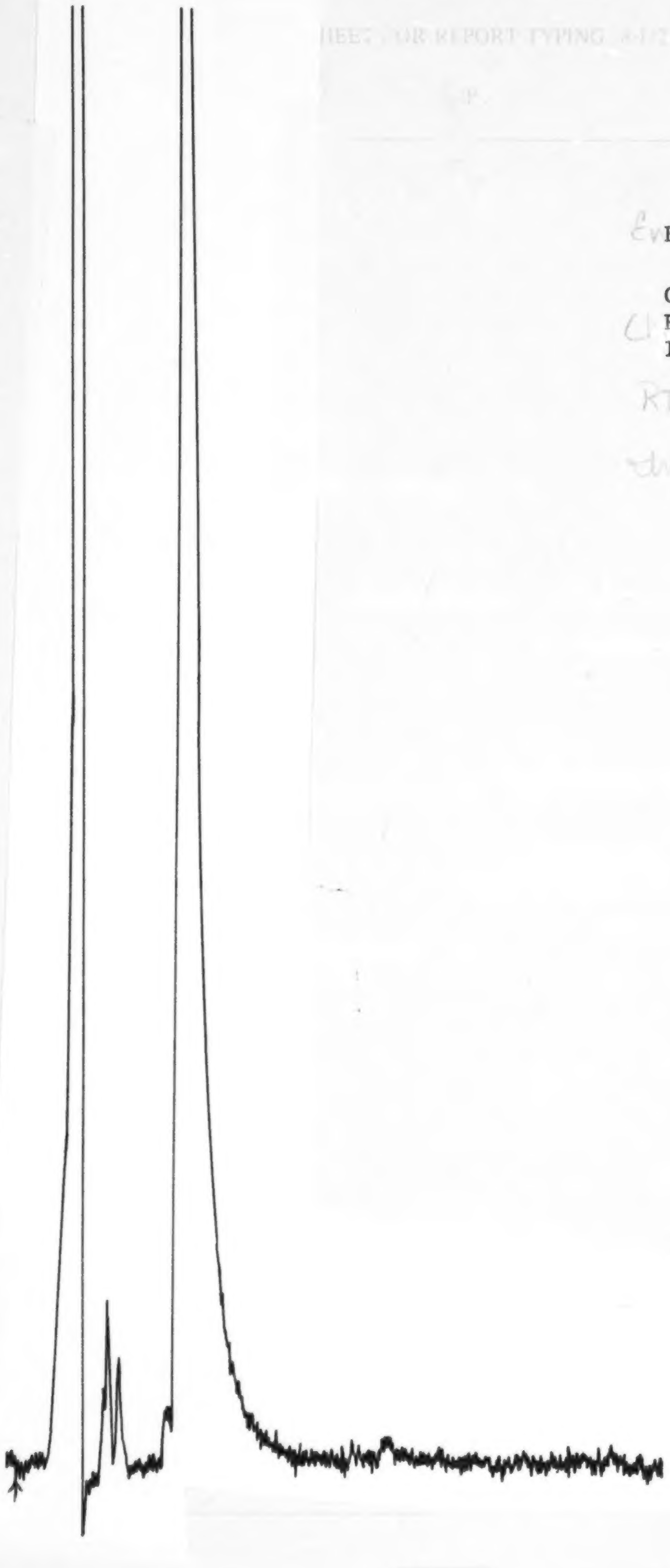
SAMPLE 1
SPIKE
Chromatographic System E-125
RI 2X
Injection volume 100ul

30 Lines to End of Typing Area

~~134a~~ 130



Environmental Sample 1
SPIKE
Chromatographic Conditions C18
RI - 2X
Injection Volume 100 μL

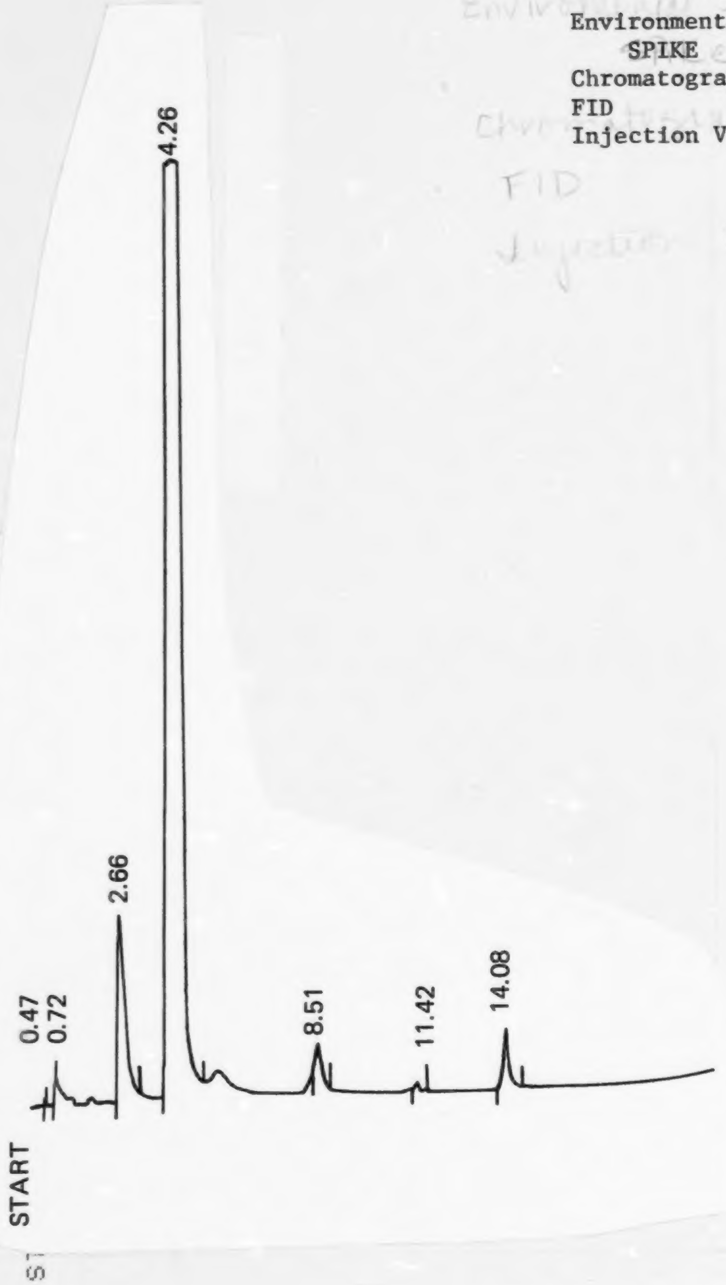


Environmental Sample 1
SPIKE
Chromatographic Conditios Phenyl
RI 2X
Injection Volume 100 µL

Environmental Sample 1
Spike
Chromatographic Conditions Phenyl
RT 2X
Injection Volume 100µl

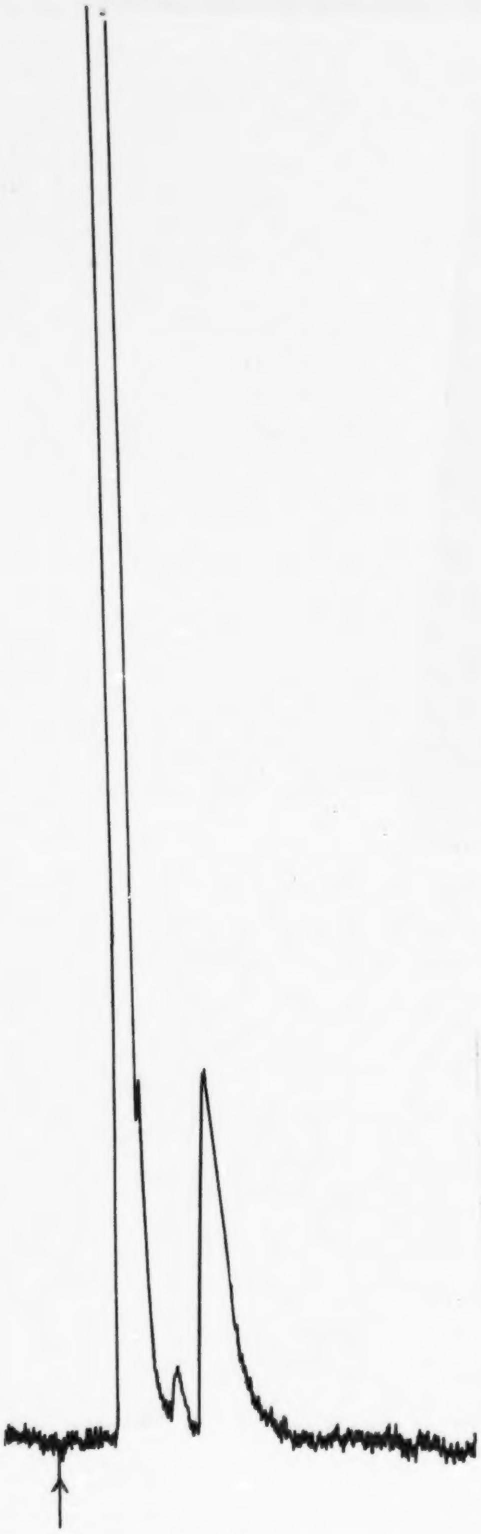
Environmental SAMPLE 1 SP
Spike
Chromatographic Conditions Tenax
FID
Injection Volume 2µl

Environmental Sample 1
SPIKE
Chromatographic Conditions Tenax
FID
Injection Volume 2 µL



10 Lines
to End of
Typing Area

For Page Numbering

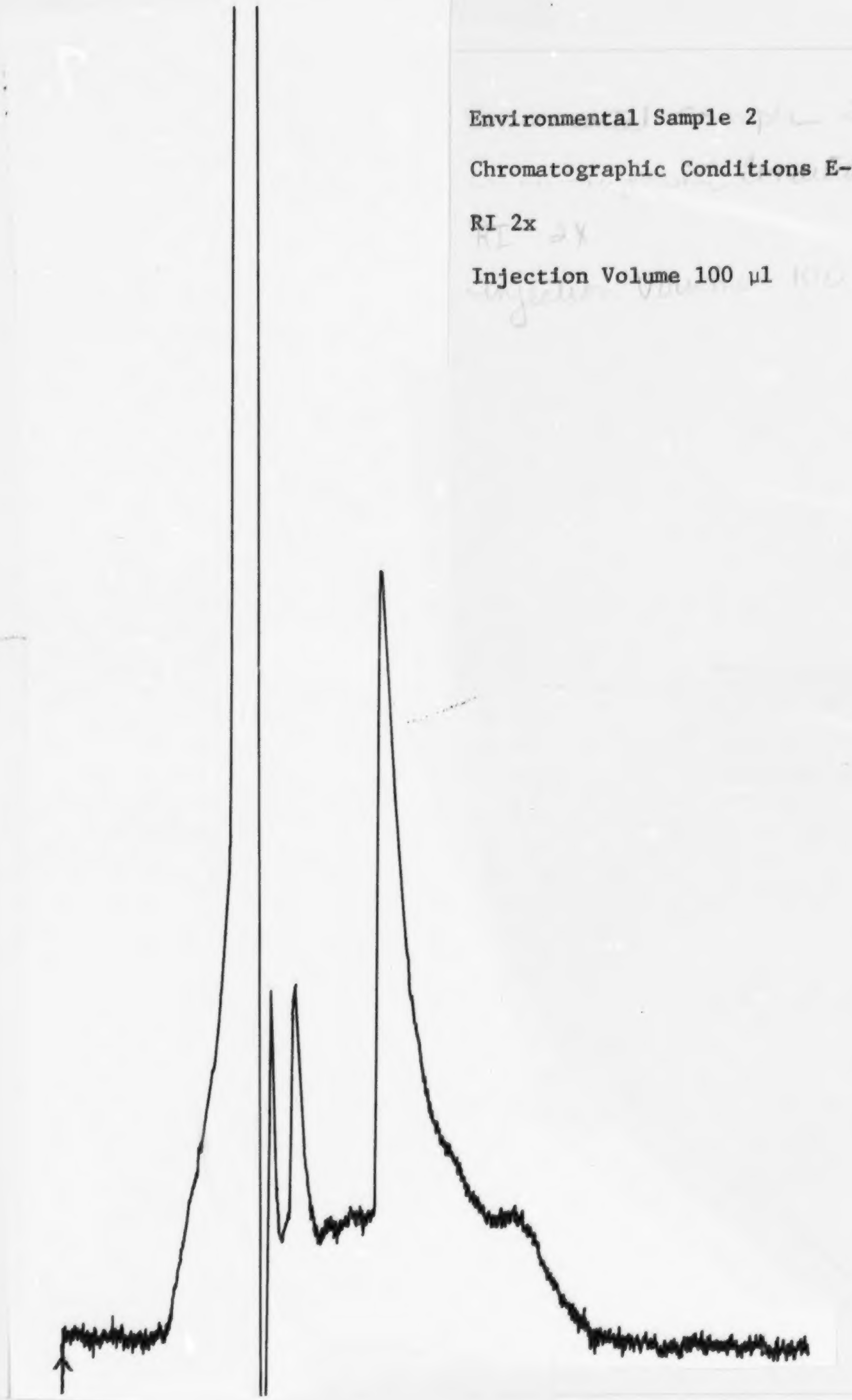


Unknown Environment Sample 2

Chromatographic System RP-2

RI 2x

Injection Volume 100 µl

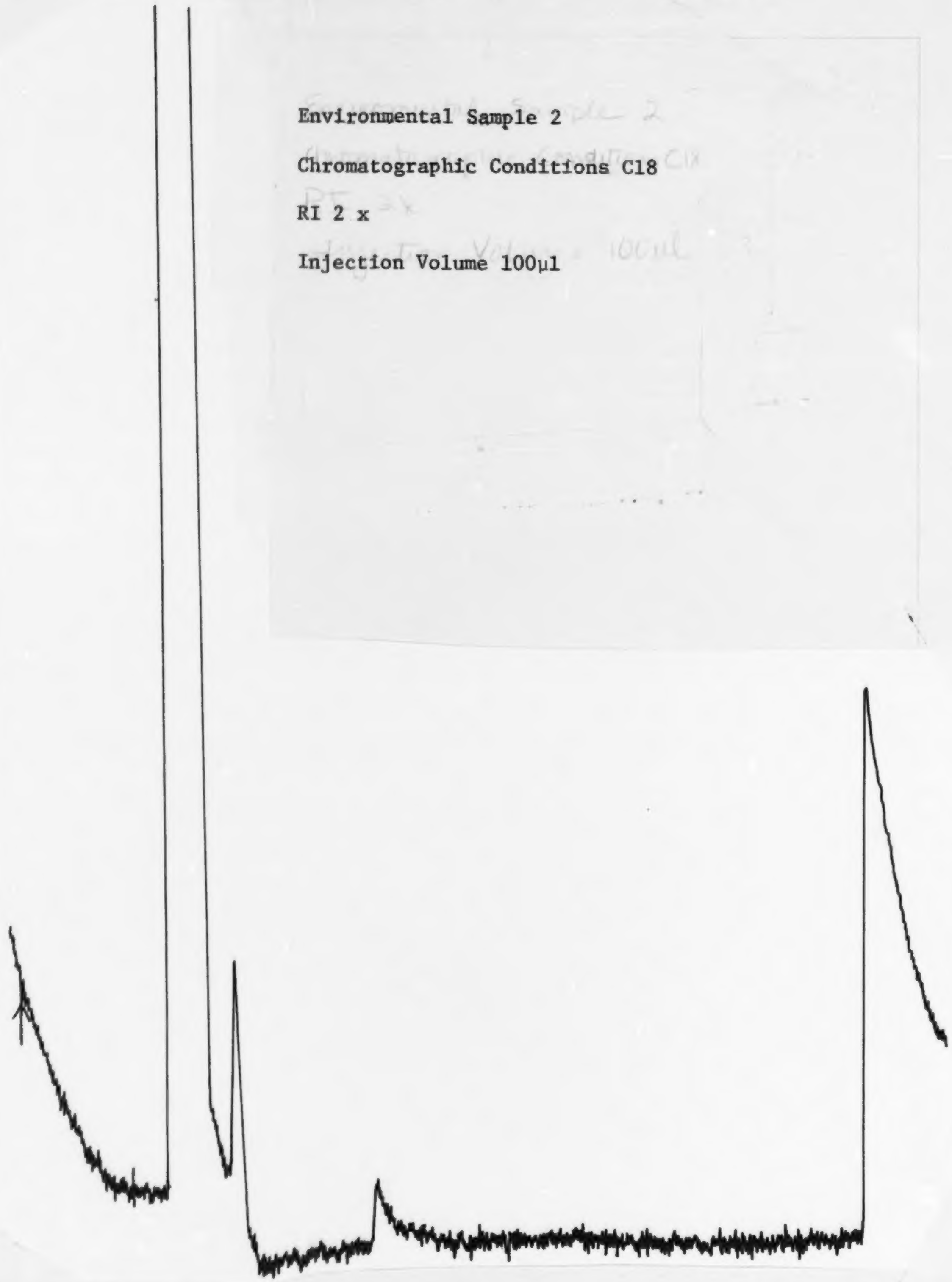


Environmental Sample 2

Chromatographic Conditions E-125

RI 2x

Injection Volume 100 µl



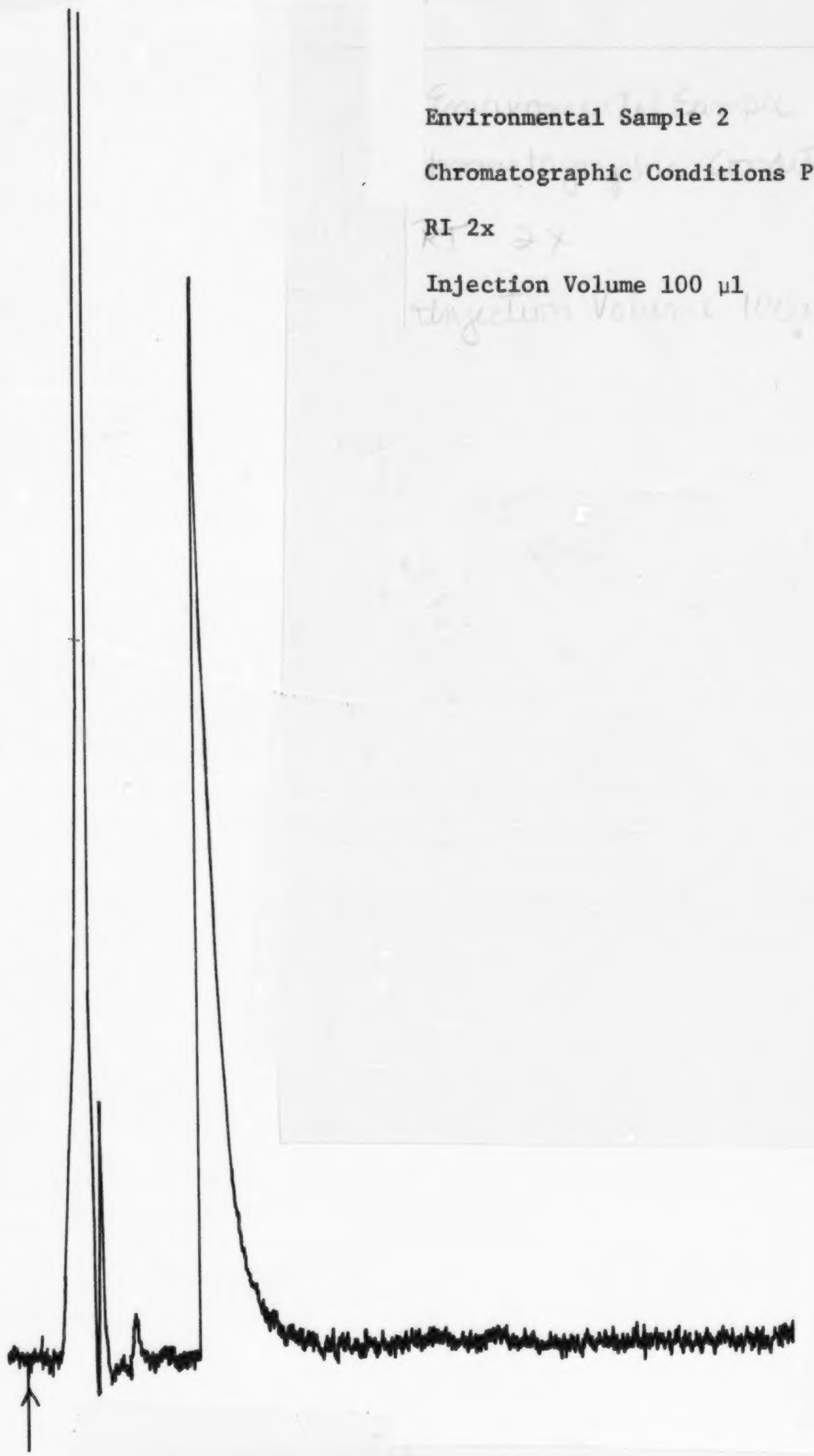
Environmental Sample 2

Chromatographic Conditions C18

RI 2 x

Injection Volume 100µl

SE THIS SHEET FOR ORT TYPING 8-1/2 x 11



Environmental Sample 2

Chromatographic Conditions Phenyl

RI 2x

Injection Volume 100 µl

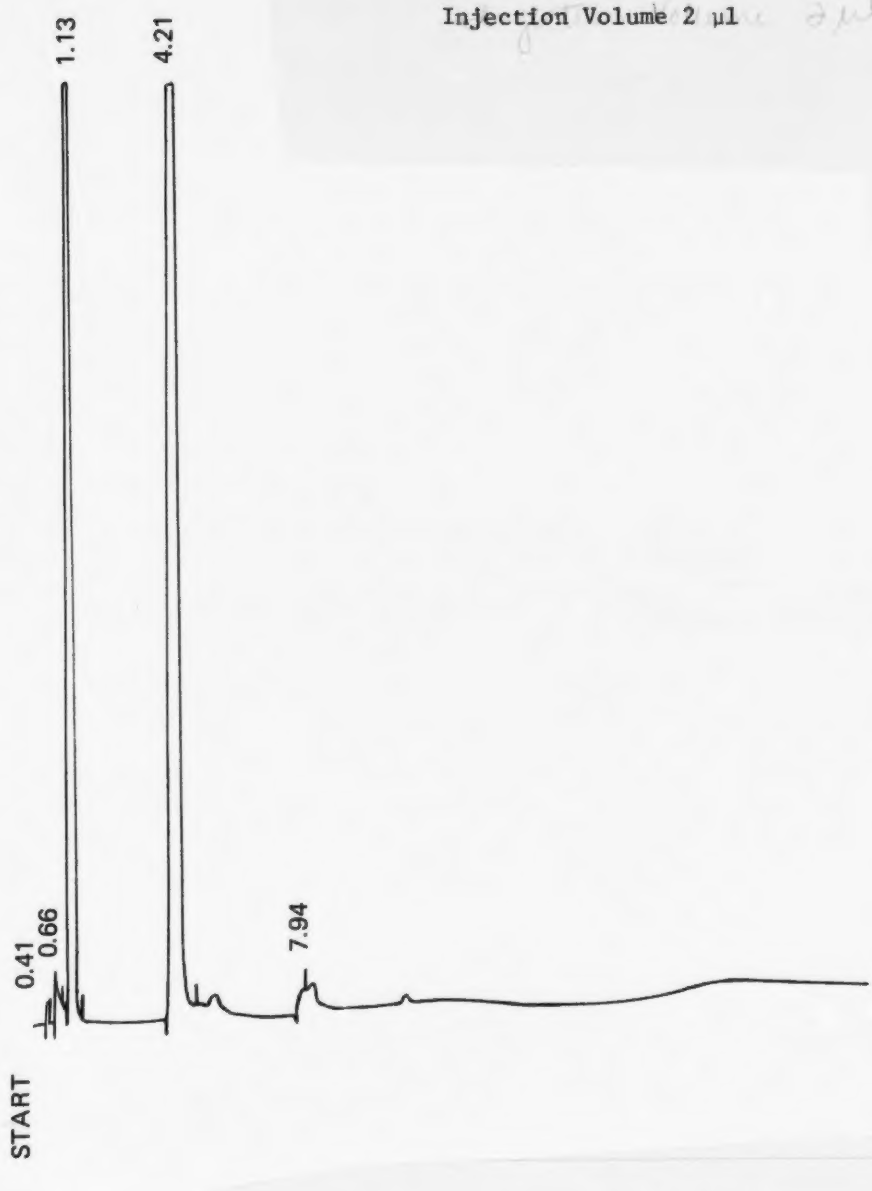
10 Lines
to End of
Typing Area

Environmental Sample 2

Chromatographic Conditions Tenax

FID

Injection Volume 2 µl



10 Lines
to End of
Typing Area

## APPENDIX 3

## IR REPORTS

**IR REPORT**

**SAMPLE:** LC1 - Fraction 1

| Wave Number (cm$^{-1}$) | Intensity | Assignment | Comments |
|---|---|---|---|
| 2850 | M | | |
| 2920 | M | aliphatic CH | |
| 2960 | Sh | | |
| 1450,1380 | w | | |
| 1650 | | water | |
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**IR REPORT**

**SAMPLE:** LC2 - Fraction 2

| Wave Number (cm$^{-1}$) | Intensity | Assignment | Comments |
|---|---|---|---|
| 32-3300 | w-broad | H-bonded OH | |
| 2960,2920 | w | aliphatic CH | |
| 2850 | | | |
| 1650 | M | water | |
| 1520 | w | | |
| 1390 | w | aliphatic CH | |
| 1110 | w | | |
| 1020 | w | C-0 of alcohols | |
| 800 | w | | |
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**IR REPORT**

**SAMPLE:** LC3

| Wave Number (cm$^{-1}$) | Intensity | Assignment | Comments |
|---|---|---|---|
| 2920,2850 | w | aliphatic CH | |
| 1650 | s | water | |
| 1520 | m | | |
| 1120 | s | C-0 of 2° alcohol | |
| 1020 | m | C-0 of 2° alcohol | |
| 620 | w | | |
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**IR REPORT**

**SAMPLE:** LC4

| Wave Number (cm$^{-1}$) | Intensity | Assignment | Comments |
|---|---|---|---|
| 2960,2920 | m | aliphatic CH | |
| 2850 | w | | |
| 1457,1380 | w | | |
| 1740 | w | C=0 of an aldehyde | |
| 1650 | s | water | |
| 1520 | m | | |
| 1120 | s | C-0 of alcohol 2° | |
| 1020 | m | C-0 of alcohol 1° | |
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**IR REPORT**

**SAMPLE:** LC5

| Wave Number (cm$^{-1}$) | Intensity | Assignment | Comments |
|---|---|---|---|
| 3350 | w | OH of alcohol | |
| 2950,2920 | s | aliphatic C-H | |
| 2850 | m | | |
| 1380,1450 | w | | |
| 1740 | w | C=0 | |
| 1650 | | water? | |
| 1520 | | | |
| 1120 | m | C-0 of 2° alcohol | polyhydric alcohol |
| 1090 | m | | |
| 1020 | m | C-0 of 1° alcohol | |
| | | | |
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**IR REPORT**

**SAMPLE:** LC6

| Wave Number (cm$^{-1}$) | Intensity | Assignment | Comments |
|---|---|---|---|
| 3350 | vw | OH of alcohol | |
| 2920,2850 | w | aliphatic CH | |
| 1740 | w | C=0 of aldehyde | |
| 1650 | m | water | |
| 1560 | w | | |
| 1540 | w | | |
| 1380 | m | CH - bend | |
| 1200 | m | glucose? | |
| 1190 | w | | |
| 1120 | s | C-0 of polyhydric alcohols | |
| 1070 | m | | |
| 1030 | m | | |
| 1610 | vw | ring mode from phenol? | |

**IR REPORT**

**SAMPLE:** LC7

| Wave Number (cm⁻¹) | Intensity | Assignment | Comments |
|---|---|---|---|
| 3350 | s | OH from alcohol | |
| 2920,2870 | m | aliphatic CH | |
| 1100 | m | 2° alcohol | |
| 1200 | vw | phenol | |
| 1030 | m | 1° alcohol | |
| 920 | | | |
| 850 | | | |
| This spectrum is almost identical to glycerol | | | |
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**IR REPORT**

**SAMPLE:**

| Wave Number (cm⁻¹) | Intensity | Assignment | Comments |
|---|---|---|---|
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# APPENDIX 4

## LRMS Reports and Organic Extract Summary Table

**LRMS REPORT**

**SAMPLE:** WATER SOLUBLES LC5

**Major Categories**

| Intensity | Category | MW Range |
|---|---|---|
| 100 | UNCLASSIFIED * | To 414 |
| 10 | ESTERS * | — |
| | | |
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**Sub-Categories, Specific Compounds**

| Intensity | Category | m/e | Composition |
|---|---|---|---|
| 10 | PHTHALATES | — | — |
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**Other**

*NOTE THAT THE TOTAL OBSERVED MATERIAL WAS VERY SMALL, AND MAY ALL BE DUE TO ARTIFACTS. MOST OF THE OBSERVED MATERIAL WAS ALIPHATIC IN NATURE

**LRMS REPORT**

**SAMPLE:** WATER SOLUBLES LC6

**Major Categories**

| Intensity | Category | MW Range |
|---|---|---|
| 100 | ALCOHOLS | 92 |
| 10 | PHENOLS | 94 |
| 10 | ESTERS | 390 |
| | | |
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| | | |

**Sub-Categories, Specific Compounds**

| Intensity | Category | m/e | Composition |
|---|---|---|---|
| 100 | PROPANETRIOL (GLYCOL) | 92 | $C_3H_8O_3$ |
| 10 | PHENOL | 94 | $C_6H_6O$ |
| 10 | PHTHALATES | 278-390 | $C_{16}H_{22}O_4$ -<br>$C_{24}H_{38}O_4$ |
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**Other**

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**LRMS REPORT**

**SAMPLE:** WATER SOLUBLES LC 7

**Major Categories**

| Intensity | Category | MW Range |
|---|---|---|
| 100 | ALCOHOLS | 92 - 180 |
| 5 | AMINES | 105 |
| 10 | UNCLASSIFIED | 118 |

**Sub-Categories, Specific Compounds**

| Intensity | Category | m/e | Composition |
|---|---|---|---|
| 100 | PROPANETRIOL (GLYCOL) | 92 | $C_3H_8O_3$ |
| 10 | GLUCOSE | 180 | $C_6H_{12}O_6$ |
| 10 | DIETHANOL AMINE | 105 | $C_4H_{11}NO_2$ |

**Other**

10 UNCLASSIFIED PEAK AT m/z 118 – POSSIBLY BENZIMIDAZOLE, $C_7H_6N_2$ MW 118.

## ORGANIC EXTRACT SUMMARY TABLE

Sample Water Soluble model Compound mixture

| | LC1 | LC2 | LC3 | LC4 | LC5 | LC6 | LC7 | Σ |
|---|---|---|---|---|---|---|---|---|
| Total Organics, mg | | | | | | | | |
| TCO, mg | | | | | | | | |
| GRAV, mg | | | | | | | | |

Category Assigned Intensity MG/

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Esters (Phthalates) | | | | | 10/ | 10/ | | |
| Alcohols | | | | | | 100/ | 100/ | |
| Phenol | | | | | | 10/ | | |
| Amines | | | | | | | 10 | |
| Carbohydrates (Glucose) | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| Unclassified (aliphatic | | | | | 100/ | | | |
| materials) | | | | | | | | |
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